

Europäisches Patentamt

**European Patent Office** 

Office européen des brevets



(11) EP 1 094 101 A2

(12)

# **EUROPEAN PATENT APPLICATION**

(43) Date of publication: 25.04.2001 Bulletin 2001/17

(51) Int. Cl.<sup>7</sup>: **C09K 11/06**, H05B 33/14

(21) Application number: 00203504.6

(22) Date of filing: 09.10.2000

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 20.10.1999 US 421980

(71) Applicant: EASTMAN KODAK COMPANY Rochester, New York 14650 (US) (72) Inventors:

Shi, Jianmin,
 c/o Eastman Kodak Company
 Rochester, New York 14650-2201 (US)

Zheng, Shiying,
 c/o Eastman Kodak Company
 Rochester, New York 14650-2201 (US)

(74) Representative:

Lewandowsky, Klaus, Dipl.-Ing. et al Kodak Aktiengesellschaft, Patentabteilung 70323 Stuttgart (DE)

# (54) Electroluminescent devices having naphthylanthracene-based polymers

(57) An electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracene-based polymers of the following formula:

wherein:

R,  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are each individually hydrogen, or alkyl, or alkoxy of from 1 to 24 carbon atoms; aryl or substituted aryl of from 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl of from 4 to 40 carbons; or F, Cl, or Br; or a cyano group; or a nitro group;

X is a linking group; and

Y includes one or more comonomer units that are a substituted or unsubstituted alkyl, alkenyl, aryl, or heteroaryl or a conjugated group.

Printed by Xerox (UK) Business Services 2.16.7 (HRS)/3.6

### Description

[0001] The present invention relates to electroluminescent (EL) devices. More specifically, naphthylanthracene-based polymers used as luminescent materials in polymer EL devices.

[0002] Electroluminescent devices are opto-electronic devices where light emission is produced in response to an electrical current through the device. The physical model for EL is the radiative recombination of electrons and holes. The term light emitting diode (LED) is commonly used to describe an EL device where the current-voltage behavior is non-linear, meaning that the current through the EL device is dependent on the polarity of the voltage applied to the EL device. Both organic and inorganic materials have been used for the fabrication of LEDs. Inorganic materials such as ZnS/Sn, Ga/Bs, Ga/As have been used in semiconductor lasers, small area displays, LED lamps, and so forth. However, the drawbacks of inorganic materials include difficulties to process and to obtain large surface areas and efficient blue light.

[0003] Organic polymers used as light-emitting materials in EL devices offer several advantages over inorganic materials, such as simpler manufacturing, low operating voltages, the possibility of producing large area and full-color displays. Conjugated polymers such as poly(phenylvinylene) (PPV) were first introduced as EL materials by Burroughes and others in 1990 (Burroughes, J. H. Nature 1990, 347, 539-41). Considerable progress has been made since then to improve the stability, efficiency, and durability of polymeric LEDs (Sheats, J. R. and others Science 1996, 273, 884-888; Berggren, M. and others Nature 1994, 372, 444-6; Holmes, A. B. and others WO 94/29883 (1994); and Spreitzer. and others, Adv. Mater. 1998, 10(16), 1340). Polymers with wide energy bandgap to emit blue light are important materials because stable, efficient blue-light-emitting materials with high brightness are desirable for full color EL display applications. With these primary materials, it is possible to produce other colors by a downhill energy transfer process. For instance, a green or red EL emission can be obtained by doping a blue EL host material with a small amount of green or red luminescent material.

[0004] Incorporating non-conjugated spacer groups into a conjugated polymer backbone is an effective approach to break conjugation thus increasing energy bandgap in order to emit blue light. These spacer groups usually prevent the extended conjugation and contribute to the solubility and film-forming properties of the polymer. Blue-light-emitting PPV (Aguiar, M and others *Macromolecules* 1995, 28, 4598-602), polythiophene (Andersson, M. R. and others *Macromolecules* 1995, 28, 7525-9), and PPP (Hilberer, A and others *Macromolecules* 1995, 28, 4525-9) have been prepared by this approach. However, such spacer group can act as a barrier to the injection and mobility of the charge carriers which leads to high threshold voltages and operating voltages. Thus, it is desirable to develop processable new blue-light-emitting polymers with low driving voltages for full color display.

[0005] It is an object of the present invention to provide wide energy bandgap luminescent polymeric materials useful for polymer EL devices.

[0006] It is a further object of the present invention to provide wide energy bandgap luminescent polymers which emit blue light.

[0007] These objects are achieved in an electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracene-based polymers of formula (I).

$$R_1$$
 $R_2$ 
 $R_2$ 
 $R_3$ 
 $R_2$ 

**(I)** 

wherein:

35

40

45

50

55

 $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are each individually hydrogen, or alkyl, or alkoxy of from 1 to 24 carbon atoms; aryl or substituted aryl of from 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl of from 4 to 40 carbons; or F, Cl, or Br; or a cyano group; or a nitro group;

X is a linking group; and

Y includes one or more comonomer units that are a substituted or unsubstituted alkyl, alkenyl, aryl, or heteroaryl

or a conjugated group.

10

15

20

30

35

40

45

50

[0008] The present invention provides polymeric luminescent materials with a number of advantages which include good solubility and better thermal stability. With the primary wide energy bandgap chromophore, 9,10-di-(2-naphthyl)anthracene, other color emitting luminescent copolymers can be easily designed and produced by introducing the narrow energy bandgap chromorphores into the polymeric chain.

- FIG. 1 illustrates in cross-section a bi-layer EL device which can use a polymer in accordance with the present invention;
- FIG. 2 illustrates a cross-section of a modified bi-layer EL device which can use a polymer in accordance with the present invention;
- FIG. 3 illustrates a cross-section of a single-layer EL device which can use a polymer in accordance with the present invention;
- FIG. 4 illustrates the absorption and photoluminescence spectra of polymer 26 and eletroluminescence spectrum of single-layer EL device fabricated from polymer 26;
- FIG. 5 illustrates the absorption and photoluminescence spectra of polymer 28 and eletroluminescence spectrum of single-layer EL device fabricated from polymer 28; and
- FIG. 6 illustrates the voltage-current density and luminance characteristics of a single-layer EL device fabricated from polymer 28.

[0009] The present invention provides light-emitting polymers containing 9,10-di-(2-naphthyl)anthracene with good solubility and thermal stability as shown in formula I. The chromophore 9,10-di-(2-naphthyl)anthracene has been shown to be particularly useful for the fabrication of efficient and stable EL devices as disclosed in commonly-assigned US-A-5,935,721 by Shi and others. Furthermore, 9,10-di-(2-naphthyl)anthracene chromophore has a wide energy bandgap. The energy bandgap is the energy difference between the energy level of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Incorporation of the second comonomer unit Y can serve several purposes:

- (1) to further improve solubility of the polymer;
- (2) to improve electron or hole transporting ability; and
- (3) to tune the emissive color of the polymer.

[0010] Therefore, the second comonomer unit Y can be the groups to improve solubility, or electron or hole transporting mobility, or emissive moiety with narrow energy bandgap. The green- or red-light-emitting polymer can be obtained through intramolecular energy downhill transfer.

[0011] The polymer shown in formula I is a polymer containing a 9,10-di-(2-naphthy)anthracene, wherein:

 $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are each individually hydrogen, or alkyl or alkoxy containing 1 to 24 carbon atoms; aryl or substituted aryl of containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons; or F, CI, or Br; or a cyano group; or a nitro group. For example,  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  may represent hydrogen, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tbutyl, pentyl, hexyl, ethylhexyl, heptyl, octyl, nonyl, decyl, dodecyl, hexyadecyl, cyclohexyl, cyclopentyl, methoxy, ethoxy, butoxy, hexyloxy, ethylhexyloxy, methoxyethoxyethyl, methoxyethyloxyethoxyethyl, phenyl, tolyl, nathphyl, xylene, anthracene, phenanthrene, phenylmethylenephenyl, benzyl, phenoxy, pyridyl, thiophenyl. Preferably,  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are hydrogen, t-butyl, phenyl, 2-ethylhexyloxy, or 4-methoxypheny.

X represents a linking group and include but not limited to the following groups:

### Group I:

X is a carbon-carbon bond linking group:

$$-\overset{R}{\overset{}{\overset{}{\text{c}}}}=\overset{C}{\overset{}{\overset{}{\text{c}}}}$$

wherein R is hydrogen, or alkyl group containing 1 to 24 carbon atoms; aryl or substituted aryl of containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons; or F, Cl, or Br; or a cyano group;

Group II:

5

10

15

20

25

30

35

40

45

50

55

X is an ether or thioether linking group:

Group III:

X is an ester linking group:

Group IV:

X is an anhydride linking group:

Group V:

X is a carbonate linking group:

5

Group VI: 10

X is a sulfone or sulfine linking group:

15

25

20

Group VII:

X is an amine linking group: 30

35

wherein R is hydrogen, or alkyl group containing 1 to 24 carbon atoms; aryl or substituted aryl of containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons;

Group VIII: 40

X is an amide linking group:

50

45

55

wherein R is hydrogen, or alkyl group containing 1 to 24 carbon atoms; aryl or substituted aryl of containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons;

Group IX:

X is a urea linking group:

wherein R is hydrogen, or alkyl group containing 1 to 24 carbon atoms; aryl or substituted aryl of containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons;

Group IX:

5

10

15

20

25

35

40

45

50

55

X is an aryl linking group:

(Ar)n

wherein Ar is an aryl or substituted aryl group containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons; n is an integer of from 1 to 6.

Y represents one or more second comonomer unit, and is a substituted or unsubstituted alkyl, alkenyl, aryl, heteroaryl or other conjugated groups. When more than one group is included the groups can be different.

Alkyl groups contain 1 to 28 carbon atoms;

Substituted or unsubstituted aryl groups contain 6-28 carbon atoms which include phenyl, biphenyl, naphthyl, anthracene, fluorene, phenanthrene, spirophenyl, perylene, or pyrene groups;

Substituted or unsubstituted heteroaryl groups contain 4-40 carbon atoms which include pyridine, thiophene, pyrrole, bithiophene, furan, benzimidazole, benzoxazole, quinoxaline, phenylquinoline, dipheyloxadizaole, or carbazole;

[0012] All the substituents mentioned above include alkyl or alkoxy groups containing 1 to 24 carbon atoms, aryl or substituted aryl containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 28 carbons; or F, Cl, or Br; or a cyano group; or a nitro group.

Y can be divided into the following groups.

Group I:

Y are alkyl groups of formula (II):

wherein:

R contains 1 to 24 carbon atoms, may also contains N, S, F, Cl, or Br, or Si atoms. The following molecular structures constitute specific examples of alkyl groups

polymer 1 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, m=6 polymer 2 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=n-hexyloxy, m=4 polymer 3 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, m=6

polymer 4 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, m=6 polymer 5 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=n-hexyloxy, m=4 polymer 6 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, m=6 polymer 7 R<sub>1</sub>=R<sub>2</sub>=n-hexyl, m=8 polymer 8 R<sub>1</sub>=R<sub>2</sub>=H, m=12

polymer 9 R<sub>1</sub>=H, R<sub>2</sub>=2-ethylhexyloxy, p=4, q=3 polymer 10 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=t-butyl, p=4, q=3 polymer 11 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=t-butyl, p=4, q=5

R<sub>1</sub>
R<sub>2</sub>
O- (CH<sub>2</sub>)p- N- (CH<sub>2</sub>)p- O

polymer 12 R<sub>1</sub>=H, R<sub>2</sub>=2-ethylhexyloxy, X=O, p=6 polymer 13 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=2-ethylhexyloxy, X=O, p=4 polymer 14 R<sub>1</sub>=2-ethylhexyl, R<sub>2</sub>=t-butyl, X=S, p=4

polymer 15 R<sub>1</sub>=n-hexyoxy, R<sub>2</sub>=t-butyl, X=S, p=4

5

10

15

20

25

30

35

40

45

50

55

polymer 16 R<sub>1</sub>=H, R<sub>2</sub>=2-ethylhexyloxy, p=6

polymer 17 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=2-ethylhexyloxy, p=4

polymer 18  $R_1$ =2-ethylhexyl,  $R_2$ =t-butyl, p=4

polymer 19 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, p=4

$$\begin{array}{c|c} R_1 & (CH_2)qCH_1 \\ \hline & N-(CH_2)p-N-(CH_2)p-N \\ \hline & R_2 & \\ \hline & R_1 & \\ \hline \end{array}$$

polymer 20 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, p=4, q=3 polymer 21 R<sub>1</sub>=t-butyl, R<sub>2</sub>=2-ethylhexyl, p=4, q=5

polymer 22 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=2-ethylhexyloxy, p=4, q=5

$$R_1$$
 $R_2$ 
 $R_2$ 
 $R_1$ 
 $R_2$ 
 $R_2$ 
 $R_1$ 

polymer 23 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, m=8 polymer 24 R<sub>1</sub>=t-butyl, R<sub>2</sub>=2-ethylhexyl, m=4 polymer 25 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=2-ethylhexyloxy, m=2

(CH<sub>2</sub>)mCH<sub>3</sub>

10

5

15

20

Group II:

Y are two aryl groups connected by a linking group Z of formula (III):

polymer 26 R<sub>1</sub>=R<sub>2</sub>=H, m=11

polymer 28 R<sub>1</sub>=t-butyl, R<sub>2</sub>=H, m=11

polymer 27 R<sub>1</sub>=t-butyl, R<sub>2</sub>=2-ethylhexyl, m=7

polymer 29 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=2-ethylhexyloxy, m=5 polymer 30 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, m=11

> $-(Ar_1)-Z-(Ar_2)-$ (III)

25

30

wherein:

Ar<sub>1</sub> and Ar<sub>2</sub> are substituted or unsubstituted aromatic groups containing 6-28 carbon atoms,

Z is a divalent linking groups containing 0 to 12 carbon atoms, can contain N, Si, O, Cl, F, Br, or S atoms.

The following molecular structures constitute specific examples of above mentioned groups with formula III:

35

40

45

50

55

polymer 31 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, p=6 polymer 32 R<sub>1</sub>=R<sub>3</sub>=H, R<sub>2</sub>=2-ethylhexyloxy, p=12 polymer 33 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=R<sub>3</sub>=H, p=12 polymer 34 R<sub>1</sub>=t-butyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyl, p=6

polymer 35 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, R<sub>4</sub>=CH<sub>3</sub>, X=C polymer 36 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, R<sub>4</sub>=CF<sub>3</sub>, X=C polymer 37 R<sub>1</sub>=t-butyl, R<sub>2</sub>=2-ethylhexyloxy, R<sub>3</sub>=H, R<sub>4</sub>=CF<sub>3</sub>, R<sub>3</sub>=H, X=C polymer 38 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=H, R<sub>4</sub>=CF<sub>3</sub>, X=C polymer 39 R<sub>1</sub>=t-butyl, R<sub>2</sub>=2-ethylhexyloxy, R<sub>3</sub>=H, R<sub>4</sub>=CF<sub>3</sub>, X=Si polymer 40 R<sub>1</sub>=H, R<sub>2</sub>=2-ethylhexyloxy, R<sub>3</sub>=H, R<sub>4</sub>=CF<sub>3</sub>, X=Si

polymer 41 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, R<sub>4</sub>=CH<sub>3</sub>, X=C polymer 42 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, R<sub>4</sub>=CF<sub>3</sub>, X=C polymer 43 R<sub>1</sub>=t-butyl, R<sub>2</sub>=2-ethylhexyloxy, R<sub>3</sub>=H, R<sub>4</sub>=CF<sub>3</sub>, X=Si polymer 44 R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=H, R<sub>4</sub>=CH<sub>3</sub>, X=C polymer 45 R<sub>1</sub>=H, R<sub>2</sub>=2-ethylhexyloxy, R<sub>3</sub>=H, R<sub>4</sub>=CF<sub>3</sub>, X=Si

polymer 46 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=R<sub>4</sub>=CH<sub>3</sub> polymer 47 R<sub>1</sub>=R<sub>2</sub>=H, R<sub>3</sub>=R<sub>4</sub>=CH<sub>3</sub> polymer 48 R<sub>1</sub>=H, R<sub>2</sub>=2-ethylhexyloxy, R<sub>3</sub>=n-butyl, R<sub>4</sub>=CH<sub>3</sub>

$$\begin{bmatrix} R_2 & 0 & R_4 & R_3 & 0 \\ R_2 & R_3 & R_4 & R_3 & R_4 \end{bmatrix}$$

polymer 49 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=CH<sub>3</sub>, R<sub>4</sub>=H, X=C polymer 50 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=CH<sub>3</sub>, R<sub>4</sub>=H, X=C polymer 51 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=n-butyl, R<sub>4</sub>=H, X=Si polymer 52 R<sub>1</sub>=R<sub>2</sub>=R<sub>4</sub>=H, R<sub>3</sub>=CF<sub>3</sub>, X=C polymer 53 R<sub>1</sub>=H, R<sub>2</sub>=2-ethylhexyloxy, R<sub>3</sub>=CH<sub>3</sub>, R<sub>4</sub>=n-butyl, X=Si

polymer 54 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-butyl, R<sub>3</sub>=phenyl polymer 55 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=phenyl polymer 56 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-butyl polymer 57 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=2-ethylhexyloxy, R<sub>3</sub>=phenyl

$$\begin{bmatrix} R_1 & R_2 & 0 & R_3 & 0 \\ N-C-N & N-C-N & N-C-N & 0 \\ R_2 & R_1 & N-C-N & 0 \\ R_2 & R_3 & N-C-N & N-C-N \\ \end{bmatrix}$$

polymer 58 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyl polymer 59 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyl polymer 60 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyl polymer 61 R<sub>1</sub>=t-butyl, R<sub>2</sub>=H, R<sub>3</sub>=2-ethylhexyl polymer 62 R<sub>1</sub>=H, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=n-hexyl polymer 63 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=4-methyloxyphenyl

$$R_2$$
 $R_2$ 
 $R_2$ 
 $R_3$ 

# EP 1 094 10". A2

polymer 64 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, X=O polymer 65 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, X=S polymer 66 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, X=O polymer 67 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, X=O

5

10

15

25

20

30

35

40

45

50

55

polymer 68  $R_1$ =2-ethylhexyloxy,  $R_2$ =H,  $R_3$ = $R_4$ =n-hexyl

polymer 69  $R_1$ =n-hexyl,  $R_2$ =H,  $R_3$ = $R_4$ =n-hexyl

polymer 70  $R_1$ =t-butyl,  $R_2$ =n-hexyl,  $R_3$ = $R_4$ =4-methyloxyphenyl

polymer 71 R<sub>1</sub>=R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=R<sub>4</sub>=n-hexyl

 $\begin{bmatrix} R_1 \\ R_2 \\ R_1 \end{bmatrix}$ 

polymer 72  $R_1$ =2-ethylhexyloxy,  $R_2$ =H

polymer 73 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy

polymer 74  $R_1=R_2=n$ -hexyl

polymer 75  $R_1$ =2-ethylhexyloxy,  $R_2$ =t-butyl

polymer 76 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H

polymer 77  $R_1=R_2=n$ -hexyl,  $R_3=H$ polymer 78  $R_1=t$ -butyl,  $R_2=n$ -hexyloxy,  $R_3=H$ polymer 79  $R_1=t$ -butyl,  $R_2=R_3=n$ -hexyloxy

5

10

 $\begin{bmatrix} R_1 & R_2 & 0 \\ N-C & R_3 & 0 \\ R_2 & R_1 & C-N \end{bmatrix}$ 

15

20

polymer 80 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H polymer 81 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=n-hexyloxy polymer 82 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=H polymer 83 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyloxy

25

Y are aromatic hydrocarbons of formula (IV):

(Ar)

30

wherein:

Group III:

Ar is substituted or unsubstituted aryl groups with 6 to 28 carbon atoms.

35

The following molecular structures constitute specific examples of above mentioned groups with formula IV:

40

$$\begin{bmatrix} & & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ &$$

50

45

polymer 84 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, p=0 polymer 85 R<sub>1</sub>=R<sub>2</sub>=n-hexyl, R<sub>3</sub>=H, p=1 polymer 86 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=H, p=2 polymer 87 R<sub>1</sub>=t-butyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyloxy, p=1

polymer 88 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, m=5 polymer 89 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=H, m=17 polymer 90 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, m=7 polymer 91 R<sub>1</sub>=t-butyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyloxy, m=9

$$\begin{bmatrix} R_1 \\ R_2 \\ R_1 \end{bmatrix} = \begin{bmatrix} R_2 \\ C \\ C \end{bmatrix} = \begin{bmatrix} R_3 \\ C \\ C \end{bmatrix}$$

polymer 92 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H polymer 93 R<sub>1</sub>=R<sub>2</sub>=n-hexyl, R<sub>3</sub>=H polymer 94 R<sub>1</sub>=t-butyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyloxy polymer 95 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=H

polymer 96 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=R<sub>4</sub>=H polymer 97 R<sub>1</sub>=2-ethylhexyl, R<sub>2</sub>=R<sub>4</sub>=H, R<sub>3</sub>=n-hexyloxy polymer 98 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=n-hexyloxy, R<sub>4</sub>=H polymer 99 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyloxy, R<sub>3</sub>=R<sub>4</sub>=H

polymer 100 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=R<sub>4</sub>=H, p=q=1 polymer 101 R<sub>1</sub>=2-ethylhexyl, R<sub>2</sub>=R<sub>4</sub>=H, R<sub>3</sub>=n-hexyloxy, p=q=1 polymer 102 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=n-hexyloxy, R<sub>4</sub>=H, p=q=2 polymer 103 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyloxy, R<sub>4</sub>=H, p=q=2 polymer 104 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, R<sub>4</sub>=n-hexyl, p=q=2 polymer 105 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=R<sub>4</sub>=n-hexyloxy, R<sub>3</sub>=H, p=q=2

$$\begin{bmatrix} R_1 & R_2 & R_4 & R_5 \\ R_4 & R_5 & R_6 & R_7 \\ R_2 & R_1 & R_2 & R_5 \end{bmatrix}$$

polymer 106 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=R<sub>4</sub>=H polymer 107 R<sub>1</sub>=2-ethylhexyl, R<sub>2</sub>=R<sub>4</sub>=H, R<sub>3</sub>=n-hexyloxy polymer 108 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=n-hexyloxy, R<sub>4</sub>=H polymer 109 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyloxy, R<sub>3</sub>=R<sub>4</sub>=H

$$\begin{bmatrix} R_1 & R_2 & 0 & R_3 & 0 \\ N-C-N & N-C-N &$$

polymer 110  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ =H polymer 111  $R_1$ = $R_2$ =n-hexyl,  $R_3$ =H polymer 112  $R_1$ =t-butyl,  $R_2$ = $R_3$ =n-hexyloxy polymer 113  $R_1$ =2-ethylhexyloxy,  $R_2$ =H,  $R_3$ =n-hexyloxy

polymer 114  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ =H polymer 115  $R_1$ =2-ethylhexyloxy,  $R_2$ =n-hexyl,  $R_3$ =H polymer 116  $R_1$ =t-butyl,  $R_2$ = $R_3$ =n-hexyl

polymer 117 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H polymer 118 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=H polymer 119 R<sub>1</sub>=t-butyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyl polymer 120 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyl

polymer 121 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=H polymer 122 R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=n-hexyl polymer 123 R<sub>1</sub>=R<sub>3</sub>=2-ethylhexyloxy, R<sub>2</sub>=H

5

10

15

polymer 124  $R_1$ =2-ethylhexyloxy,  $R_2$ =n-hexyl,  $R_3$ =H

polymer 125 R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=n-hexyl

polymer 126 R<sub>1</sub>=R<sub>3</sub>=2-ethylhexyloxy, R<sub>2</sub>=H

polymer 127  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ =H

20

Y are aromatic hydrocarbons linked by a double bond of formula (V)

25

$$-Ar_1$$
 $R'$ 
 $Ar_2$ 

30

(V)

wherein:

Group IV:

Ar<sub>1</sub> and Ar<sub>2</sub> are substituted or unsubstituted aryl groups with 6 to 28 carbon atoms;

R' and R" are hydrogen, or alkyl group containing 1 to 12 carbon atoms, or CI, Br, F, or a cyano group; and p is an integer from 1 to 3.

The following molecular structures constitute specific examples of above mentioned groups with formula IV:

40

45

35

50

55

polymer 128  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ = $R_4$ = $R_5$ =H

polymer 129  $R_1$ =2-ethylhexyloxy,  $R_2$ =n-hexyl,  $R_3$ = $R_4$ = $R_5$ =H

polymer 130 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=R<sub>5</sub>=H, R<sub>4</sub>=n-hexyloxy

polymer 131 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>4</sub>=R<sub>5</sub>=H, R<sub>3</sub>=CN

polymer 132  $R_1$ =2-ethylhexyloxy,  $R_2$ =n-hexyl,  $R_3$ =CN,  $R_4$ = $R_5$ =H

5

$$\begin{bmatrix} R_1 & R_2 & R_3 & R_4 & R_5 & R_5 & R_4 & R_5 & R_5 & R_6 & R_$$

polymer 133 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H polymer 134 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H polymer 135 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=R<sub>5</sub>=H, R<sub>4</sub>=n-hexyloxy polymer 136 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>4</sub>=R<sub>5</sub>=H, R<sub>3</sub>=CN polymer 137 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=CN, R<sub>4</sub>=R<sub>5</sub>=H

polymer 138 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H polymer 139 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H polymer 140 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=R<sub>5</sub>=H, R<sub>4</sub>=n-hexyloxy polymer 141 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>4</sub>=R<sub>5</sub>=H, R<sub>3</sub>=CN polymer 142 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=CN, R<sub>4</sub>=R<sub>5</sub>=H

$$\begin{bmatrix} R_1 & R_2 & R_3 & R_4 & R_5 & R_$$

polymer 143  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ = $R_4$ = $R_5$ =H polymer 144  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_1$ = $R_2$ = $R_3$ = $R_4$ = $R_5$ = $R_5$ = $R_4$ = $R_5$ 

polymer 145  $R_1$ =t-butyl,  $R_2$ =n-hexyl,  $R_3$ = $R_5$ =H,  $R_4$ =n-hexyloxy polymer 146  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_4$ = $R_5$ =H,  $R_3$ =CN polymer 147  $R_1$ =2-ethylhexyloxy,  $R_2$ =n-hexyl,  $R_3$ =CN,  $R_4$ = $R_5$ =H

5

10

15

20

polymer 148 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H, p=q=r=1 polymer 149 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>==H, p=q=r=1 polymer 150 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=R<sub>5</sub>=H, R<sub>4</sub>=n-hexyloxy, p=q=2, r=1 polymer 151 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>4</sub>=R<sub>5</sub>=H, R<sub>3</sub>=CN, p=q=r=1 polymer 152 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=CN, R<sub>4</sub>=R<sub>5</sub>=H, p=q=r=2

30

25

40

35

polymer 153 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H, p=q=r=1 polymer 154 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H, p=q=r=1 polymer 155 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=R<sub>5</sub>=H, R<sub>4</sub>=n-hexyloxy, p=q=2, r=1 polymer 156 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>4</sub>=R<sub>5</sub>=H, R<sub>3</sub>=CN, p=q=r=1 polymer 157 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=CN, R<sub>4</sub>=R<sub>5</sub>=H, p=q=r=2

45

Group V:

Y are heteroaromatics of formula (VI)

50

(VI)

wherein:

W is substituted or unsubstituted heteroaryl groups with 4-40 carbon atoms, and at least one or more N, S, or O atoms.

The following molecular structures constitute specific examples of above mentioned groups with formula VI:

$$C = C \begin{pmatrix} R_3 \\ R_2 \\ R_2 \end{pmatrix}$$

10

polymer 158 polymer 159 polymer 160 polymer 161

20

25

30

35

40

45

50

55

polymer 158 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, p=1 polymer 159 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, p=2 polymer 160 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyl, p=1 polymer 161 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=H, p=1

polymer 162 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, R<sub>4</sub>=n-hexyl, p=1 polymer 163 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=H, R<sub>4</sub>=2-ethylhexyl, p=2 polymer 164 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyl, R<sub>4</sub>=2-ethylhexyl, p=2 polymer 165 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=n-hexyl, R<sub>4</sub>=2-ethylhexyl, p=3

polymer 166 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=H, p=r=0, q=1 polymer 167 R<sub>1</sub>=t-butyl, R<sub>2</sub>=n-hexyl, R<sub>3</sub>=R<sub>4</sub>=2-ethylhexyl, p=r=1, q=2 polymer 168 R<sub>1</sub>=R<sub>4</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, p=r=q=1 polymer 169 R<sub>1</sub>=R<sub>2</sub>=2-ethylhexyloxy, R<sub>3</sub>=R<sub>4</sub>=H, p=r=1, q=2 polymer 170 R<sub>1</sub>=t-butyl, R<sub>2</sub>=R<sub>3</sub>=2-ethylhexyloxy, R<sub>4</sub>=H, p=r=1, q=2

$$\begin{array}{c|c}
R_1 & R_2 & N & N & N & N \\
\hline
C-N & N-C & N-$$

polymer 171  $R_1$ =2-ethylhexyloxy,  $R_2$ =H,, p=q=1, X=O polymer 172  $R_1$ =2-ethylhexyloxy,  $R_2$ =H,, p=q=1, X=S polymer 173  $R_1$ =2-ethylhexyloxy,  $R_2$ =H,, p=q=1, X=n-hexyl polymer 174  $R_1$ =2-ethylhexyloxy,  $R_2$ =n-hexyl, p=q=2, X=O polymer 175  $R_1$ =2-ethylhexyloxy,  $R_2$ =n-hexyl, p=q=2, X=S

polymer 176 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyl, p=q=2, X=N-hexyl

polymer 177 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H polymer 178 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=phenyl polymer 179 R<sub>1</sub>=t-butyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyl polymer 180 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyloxy polymer 181 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=H

polymer 182  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ =H

3DOCID: <EP\_\_\_\_\_1094101A2\_I\_>

polymer 183 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=phenyl polymer 184 R<sub>1</sub>=t-butyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyl polymer 185 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyloxy polymer 186 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=n-hexyloxy, R<sub>3</sub>=H

5

10

15

20

25

30

35

40

45

50

55

polymer 187  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ =H polymer 188  $R_1$ =2-ethylhexyloxy,  $R_2$ =H,  $R_3$ =phenyl

polymer 189  $R_1$ =t-butyl,  $R_2$ = $R_3$ =n-hexyl

polymer 190 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyl

polymer 191  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ =H

polymer 192 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=phenyl

polymer 193 R<sub>1</sub>=t-butyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyl

polymer 194  $R_1$ =2-ethylhexyloxy,  $R_2$ =H,  $R_3$ =n-hexyl

$$\begin{bmatrix} R_1 & R_2 & 0 & R_3 & 0 \\ C & N & N & C \\ R_2 & R_1 & 0 & 0 \end{bmatrix}$$

polymer 195 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=methyl polymer 196 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=phenyl polymer 197 R<sub>1</sub>=t-butyl, R<sub>2</sub>=R<sub>3</sub>=n-hexyl polymer 198 R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=H, R<sub>3</sub>=n-hexyl

[0013] In formula (I), Y can be one or the combination of more than one of the above groups. The specific molecular structures can be the combination of any of the above drawn structures.

[0014] The polymerization method and the molecular weights of the resulting polymers used in the present invention are not necessary to be particularly restricted. The molecular weights of polymers are at least 1000, and preferably at least 3000. The polymers may be prepared by condensation polymerizations, preferably by cross-coupling reactions such as Pd-catalyzed Suzuki coupling (Miyaura, N. and others *Chem. Rev.* 1995, *95*, 2457), or by condensation reaction between di-(acid chloride)s with di-amines, di-alcohols or di-phenols in the presence of bases.

[0015] Suzuki coupling reaction was first reported by Miyaura and others on the coupling of aromatic boronic acid derivatives with aromatic halides Miyaura and others *Synthetic Comm.* 1981, *11(7)*, 513). Since then, this reaction has been widely used to prepared polymers for various applications (Ranger, M. and others *Macromolecules* 1997, *30*, 7686-7691; Kim, S. and others *Macromolecules* 1998, *31*, 964-974; and Ng, P. K *Macromol. Rapid Commun.* 1997, *18*, 1009-1016). A modified process was reported by Inbasekaran and others to prepare conjugated polymers for EL devices (US-A-5,777,070). According to the present invention, the above mentioned polymers were prepared by Suzuki coupling reaction of an aromatic diboronic acid ester with an aromatic dibromide. The aromatic diboronic acid esters were prepared from the corresponding dihalide treated with nBuLi and trimethylborate followed by esterification with a di-alcohol. The synthetic schemes for polymers and monomers are illustrated in Schemes 1-6.

[0016] FIG. 1 illustrates the basic structure used to construct organic EL devices. It is a bi-layer structure comprising a hole transport layer 30 and an electron transport layer 40. The electron transport layer is also the emissive layer from which electroluminescence originates. Together they form the EL medium 50. The anode is adjacent to the hole transport layer and the cathode 60 is adjacent to the electron transport layer. The substrate is layer 10. This figure is for illustration only and the individual layer thickness is not scaled according to the actual thickness.

[0017] FIG. 2 illustrates an alternative construction of the EL device. It is a modified bi-layer structure. The EL medium contains an emissive layer between the hole transport layer and the electron transport layer. This emissive layer is the layer where electroluminescence originates. Thus, layer 300 is the hole transport layer, layer 400 is the emissive layer, layer 500 is the electron transport layer, and together they form the electroluminescent medium 600. Layer 200 is the anode and layer 700 is the cathode. The substrate is layer 100. This figure is for illustration only and the individual layer thickness is not scaled according to the actual thickness.

[0018] The bi-layer EL devices are the basic structure providing high luminous efficiency and low operating voltage. Alternative EL device structures have been demonstrated to provide improved device performance. These alternative structures include features in addition to the basic bi-layer structure such as the following structure (a) hole injection layer as disclosed in US-A-4,356,429; (b) cathode modification with alkaline or alkaline halides as disclosed in US-A-5,776,622; and (c) doped emitter layer inserted between the hole transport and electron transport layer as disclosed in US-A-4,769,292.

[0019] FIG. 3 illustrates another alternative construction of an EL device. It is a single-layer structure comprising an emitting layer 3000, sandwiched between an anode 2000 and cathode 4000. The emitting layer 3000 also acts as a charge carrier layer. Thus, single layer 3000 is the electroluminescent medium. The substrate is layer 1000. This figure is for illustration only and the individual layer thickness is not scaled according to the actual thickness.

[0020] A preferred EL device structure of this invention is a single-layer structure comprising an anode, a cathode, and single layer of electroluminescent medium. This electroluminescent layer is the emissive layer, and is also capable of transporting electrons as well as holes. The principle function of this layer is to provide efficient emissive centers for electroluminescence. This layer can comprise one of the above mentioned polymers or the blend of two or more polymers, or polymers doped with one or more fluorescent dyes (FD). The fluorescent dye is usually present in an amount on the order of a few molar percent or less of the host polymer and it is sufficient to cause the EL emission to be predominantly that of the fluorescent dye. Using this method, highly efficient EL devices can be constructed. Simultaneously, the color of the EL devices can be tuned using fluorescent dyes of different emission wavelengths. By using a mixture of fluorescent dyes, EL color characteristics of the combined spectra of the individual fluorescent dyes are produced. This dopant scheme has been described in considerable detail for EL devices in US-A-4,769,292. An important criterion for choosing a fluorescent dye as a dopant capable of modifying the hue of light emission when present in a host material is a comparison of their bandgap. For efficient energy transfer from the host to the dopant molecule, a necessary condition is that the energy bandgap of the dopant is smaller than that of the host polymer. Preferred fluorescent dyes used as the dopant in the emissive layer include but are not limited to coumarins, stilbenes, distrylstibenes, anthracene derivatives, tetracene, perlenes, rhodamines, and arylamines.

[0021] The molecular structures of the preferred fluorescent dyes for the emissive layer in the EL device are listed

10

as follows:

5

10

<sup>15</sup> FD 1 R=H FD 2 R=CO<sub>2</sub>Pr-i

20

25

FD 3 R=H, R'=t-Bu FD 4 R=R'=t-Bu 30

35

FD 5

40

45

50

55 FD 6

R

"

SO<sub>3</sub>H SO<sub>3</sub>H

озн ѕозн

5

10

FD 7

15

20

FD 8 R=H
FD 9 R=Me
FD10 R=Pr-i
FD11 R=2-ethylhexyl

30

35

50

55

FD 18 R=n-hexyl FD 19 R=phenyl

**[0022]** The above mentioned polymers can be deposited as high quality transparent thin films by spin-coating or inkjet printing the polymer solutions. Preferably, the spin-coating technique is used to form layer 3000, and preferably, only one polymer is deposited as single layer of electroluminescent medium.

[0023] Preferred materials for use in forming the cathode of the EL devices of this invention are Mg, Li, or alloys of these materials as disclosed in US-A-5,429,884 and US-A-5,776,622.

# **EXAMPLES**

10

20

25

30

35

40

45

50

55

[0024] The invention and its advantages are further illustrated by the following specific examples:

# **Synthesis of Monomers**

[0025] Monomers to be used in the present invention are not necessary to be particularly restricted. Any monomers can be used as long as the polymer formed is a polymer which satisfies the general formula (1). Typical monomer and polymer synthesis is illustrated in Schemes 1-6.

# Scheme 1

97%

9?%

Scheme 2

# Scheme 3

# Scheme 4

# Scheme 5

$$CIOC-R-COCI + HO-R-OH \xrightarrow{base} Polymer$$

# Scheme 6

20

25

30

35

40

45

### Example 1: synthesis of 1,3-di(2-(6-bromonaphthoxy))-2-propanol (compound 1)

[0026] 6-Bromo-2-hydroxy-naphthalene (66.7 g, 0.299 mol) and NaOH (7.4 g, 0.185 mol) were suspended in 500 mL of dioxane and heated for half hour until the reaction became homogeneous. Epichlorohydrin (11.5 g, 0.124 mol) was added dropwise and the reaction was heated at reflux for 20 h. The brown reaction mixture was poured into 1 L of water and the gray precipitated was filtered, washed with water and methanol, and dried under vacuum. The crude product was then recrystallized from acetone to give 41.3 g of pure product (67% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 4.28-4.35 (m, 5H), 4.50-4.55 (m, 1H), 7.15 (d, J = 2.2 Hz, 2H), 7.18 (dd, J<sub>1</sub> = 8.9 Hz, J<sub>2</sub> = 2.4 Hz, 2H), 7.48 (dd, J<sub>1</sub> = 8.7 Hz, J<sub>2</sub> = 1.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.9 Hz, 2H), 7.91 (d, J = 1.1 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 66.07, 67.87, 105.32, 115.04, 118.36, 126.84, 127.04, 127.70, 127.76, 128.24, 131.32, 155.40; M.p. 148-150 °C; FD-MS: m/z 500 (M<sup>+</sup>).

# Example 2: synthesis of 1,3-di(2-(6-bromonaphthoxy))-2-dodecyloxypropane (compound 2)

[0027] To a 500 mL round-bottomed flask were added 1,3-di(2-(6-bromonaphthoxy))-2-propanol compound 1 (30.0 g, 0.060 mol), NaOH (7.2 g, 0.18 mol), NaHSO<sub>4</sub> (20.4 g, 0.060 mol), 1-bromododecane (44.9 g, 0.18 mol), water 30 mL, and THF 160 mL. The reaction was heated under reflux for two days. After cooling to room temperature, 250 mL of water was added, and the reaction was extracted with ether (6x200 mL). The organic phase was combined, dried over MgSO<sub>4</sub>, and concentrated. The crude product was purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>/hexane (15/85) as eluent to give pure product as white powder 25.2 g (63% yield).  $^{1}$ H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 0.87 (t, J = 6.9 Hz, 3H), 1.25 - 1.39 (m, 18H), 1.60 - 1.70 (m, 2H), 3.73 (t, J = 6.6 Hz, 2H), 4.13 -4.18 (m, 1H), 4.26 -4.37 (m, 4H), 7.16 (d, J = 2.2 Hz, 2H), 7.19 (dd, J1 = 8.9 Hz, J2 = 1.8 Hz, 2H), 7.48 (dd, J<sub>1</sub> = 8.8 Hz, J<sub>2</sub> = 1.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.9 Hz, 2H), 7.91 (d, J = 1.4 Hz, 2H);  $^{13}$ C NMR (CDCl<sub>3</sub>): 14.10, 22.67, 26.05, 29.33, 29.44, 29.61, 29.65, 30.03, 31.90, 67.76, 71.16, 76.40, 106.95, 117.22, 119.85, 128.35, 128.51, 129.64, 130.13, 132.94, 156.92. M.p. 99-101 °C; FD-MS: m/z 668 (M<sup>+</sup>).

### Example 3: synthesis of bis-2,2-dimethyltrimethylene diboronate (compound 3):

### [0028]

30

35

40

45

Step 1: synthesis of diboronic acid: Bisbromide compound 2 (12.0 g, 0.018 mol) was dissolved in 150 mL of anhydrous THF and cooled to -78 °C. To this solution was added slowly nBuLi solution (33.8 mL, 1.6 M in hexane, 0.054 mol) to keep temperature lower than -60 °C. The mixture was stirred at -78 °C for 1 h and trimethyl borate (8.1 mL, 0.072 mol) was added slowly. The reaction mixture was slowly warmed up to room temperature and stirred at room temperature overnight. The reaction was quenched with dilute HCl solution and stirred under nitrogen for 1 h. The reaction mixture was then extracted with ether 5 times and dried over MgSO<sub>4</sub>. Solvent was evaporated and the crude product was used for preparation of diboranate without purification.

Step 2: Synthesis of bis-2,2-dimethyltrimethylene diboranate. The crude diboronic acid and 2,2-dimethylporpane-1,3-diol (neopentyl glycol) (3.8 g, 0.037 mol) were dissolved in toluene and heated under vigorous reflux under a Dean-Stark trap. After the completion of the reaction, toluene was evaporated and the crude product was recrystallized from hexane as off-white needle-like crystals, 7.7 g (57% yield).  $^1$ H NMR (CDCl<sub>3</sub>)  $^5$  (ppm): 0.85 (t, J = 6.9 Hz, 3H), 1.02 (s, 12H), 1.24 - 1.34 (m, 18H), 1.58 - 1.65 (m, 2H), 3.71 (t, J = 6.6 Hz, 2H), 3.79 (s, 8H), 4.11 - 4.16 (m, 1H), 4.24 - 4.36 (m, 4H), 7.17 (s, 2H), 7.14 (d, J = 8.5 Hz, 2H), 7.67 (dd, J = 8.2 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.8 (d; J = 8.3 Hz, 2H), 7.91 (s, 2H);  $^{13}$ C NMR (CDCl<sub>3</sub>): 14.11, 21.93, 22.68, 26.07, 29.35, 29.47, 29.63, 29.66, 30.06, 31.92, 67.83, 71.15, 72.37, 76.47, 106.77, 118.61, 125.77, 128.62, 130.26, 130.66, 134.80, 136.13, 157.38. M.p. 59-61.°C; FD-MS: m/z 726 (M†).

### 50 Example 4: synthesis of 4-t-butyl-2-benzoylbenzoic acid (compound 4)

[0029] 4-t-Butyl-phthalic anhydride (36.0 g, 176 mmol) and t-butyl benzene were placed under nitrogen in a 3-neck round-bottom flask equipped with a condenser. The condenser was attached to a water-gas trap for HCl released during the reaction. AlCl<sub>3</sub> (56.0 g, 420 mmol) was added in portions during which time the mixture turned dark brown. Stirring became difficult in the thick mixture. The reaction was heated at 70 °C for 1 h and then cooled to room temperature. Ice was added slowly to the flask followed by concentrated HCl solution. A large clump of solid stuck to the bottom of the flask. This was washed multiple times with water and then dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to give an oily solid. Hexane was added and after sonication, a blue-white solid was collected

by filtration. Drying gave product as white solid 32.0 g (54% yield).  $^{1}$ H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 1.33 (s, 18 H), 7.30 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.63-7.70 (m, 3H), 8.08 (s, 1H);  $^{13}$ C NMR (CDCl<sub>3</sub>): 30.98, 34.92, 125.36, 125.41, 127.78, 127.84, 128.02, 129.51, 129.60, 129.81, 134.56, 139.83, 152.94, 156.80, 170.80, 196.89.

### 5 Example 5: synthesis of 2,6/2,7-di-t-butyl-anthraquinone (compound 5)

[0030] 4-t-Butyl-2-benzoylbenzoic acid 4 (32.0 g, 95 mmol) was placed into a round-bottom flask and oleum (30%, 290 mL) was then added. The reaction mixture turned black and the reaction temperature was increased to 120° C and stirred for 3 h. The mixture was then poured into ice. The aqueous mixture was extracted using  $CH_2Cl_2$  (5x), dried over  $Na_2SO_4$  and concentrated to give a dark solid. This solid was passed through a silica gel column using  $CH_2Cl_2$  as eluent. After concentrating, the yellow-brown solid was recrystallized from hexane to give product as yellow crystals 21.0 g (69% yield).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  (ppm): 1.42 (s, 18H), 7.80 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.2 Hz), 8.20 (d, J = 8.2 Hz, 1H), 8.31 (s, 2H);  $^{13}C$  NMR ( $CDCl_3$ ): 31.01, 35.58, 123.83, 123.90, 127.17, 127.28, 131.08, 131.15, 131.34, 131.42, 133.40, 133.49, 157.94, 158.05, 182.76, 183.28,183.78

# Example 6: synthesis of 2,6/2,7-di-t-butyl-anthracene (compound 6)

[0031] 2,6-Di-t-butyl-anthraquinone 5 (10.0 g, 313 mmol), tin (18.0 g, 151 mmol), and 50 mL of glacial acetic acid were added to a round-bottom flask and heated to reflux. During heating, the anthraquinone 5 went into solution and a new solid started to precipitate out. After 3 h, TLC showed all starting material 5 disappeared. After cooling to room temperature, the mixture was poured into ice and stirred for 30 minutes. CH<sub>2</sub>Cl<sub>2</sub> was added and after separation, the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to yield a sticky, oily solid. This was used without further purification in the subsequent reaction.

[0032] The oily solid was dissolved in 110 mL of isopropyl alcohol and of NaBH<sub>4</sub> (13.0 g, 333 mmol) was added in portions. The reaction was refluxed overnight. TLC indicated the completion of the reaction. After cooling to room temperature and the reaction was neutralized with HCl (6 M) solution during which time a solid precipitated out of solution. Additional water was added and the product was collected by vacuum filtration, washed thoroughly with water and dried in an oven to give 8.8 g product (97% yield).). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 1.43 (s, 18H), 7.48-7.53 (m, 2H), 7.85-7.91 (m, 2H), 8.26-8.30 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 30.98, 34.89, 122.17, 122.25, 124.51, 124.70, 124.91, 125.36, 125.80, 127.71, 127.77, 130.05, 130.45, 131.55, 131.96, 147.23, 147.43.

# Example 7: synthesis of 2,6/2,7-di-t-butyl-9,10-dibromoanthracene (compound 7)

[0033] 2,6-Di-t-butyl-anthracene 6 (4.0 g, 13.8 mmol) was dissolved in 150 mL CCl<sub>4</sub> and then bromine (1.42 mL; 27.6 mmol) was added dropwise. After stirring at room temperature overnight, TLC indicated the completion of the reaction. The reaction mixture was poured into water and a concentrated solution of sodium thiosulfate was added. After stirring for 60 minutes, the layers were separated, the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x) and the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to give a yellow solid. This solid was recrystallized from EtOH to give pure product 6.0 g (97% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 1.48 (s, 18H), 7.69-7.71(m, 2H), 8.45-8.51 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 30.88, 35.28, 122.59, 122.93, 126.87, 128.00, 128.08, 129.88, 130.64, 149.77; M.p. 150-152 °C; FD-MS: m/z 368 (M\*).

### Example 8: synthesis of di-(2-(6-methoxynaphthyl)anthracene (compound 8)

45 [0034] Magnesium turnings (5.55 g, 231 mmol), 30 mL THF, and two crystals of iodine were placed into a round-bottomed flask under nitrogen. The flask was heated to 50 °C and dibromoethane was used to help initiate the Grignard reaction. 2-Bromo-6-methoxy naphthalene (50.0 g, 211 mmol) in 400 mL of THF was added dropwise over 90 minutes during which time heat was increased to allow for gentle reflux. After addition, the reaction mixture was allowed to reflux for an additional 2 hours.

[0035] 9,10-Dibromoanthracene (23.63 g, 70.3 mmol), 300 mL of THF and a catalytic amount of dichlorobis(triphenylphosphine)palladium (II) were all placed under nitrogen in a round bottomed flask. The Grignard reagent prepared above was then added via a double-end needle transfer while still warm. After the addition, the reaction mixture was allowed to reflux overnight. After cooling to room temperature, the precipitated solid was collected by vacuum filtration and washed with ether, THF, and water. The collected solid was placed into a beaker and HCl (6M) was added followed by ethanol. This mixture is stirred for 60 minutes and the solid is again collected by vacuum filtration. The product was washed until the washings are neutral. After drying, the solid is refluxed gently in  $CH_2CI_2$  for 60 minutes. The pure product was filtered and dried to give 85.2 g solid (82% yield) (AA8790-34). <sup>1</sup>H NMR (CDCI<sub>3</sub>)  $\delta$  (ppm): 3.97 (s, 6H), 7.29 (dd,  $J_1 = 8.9$  Hz,  $J_2 = 2.4$  Hz, 2H), 7.40 (d,  $J_1 = 8.9$  Hz, 2H), 7.53 (d,  $J_2 = 2.2$  Hz, 2H), 7.57 (d,  $J_3 = 8.0$ 

Hz, 2H), 7.64 (d, J = 6.8 Hz, 2H), 7.65 (d, J = 6.8 Hz, 2H), 7.94 (d, J = 9Hz, 2H), 7.97 (s, 2H), 8.10 (d, J = 8.4 Hz, 2H); FD-MS: m/z 490 (M<sup>+</sup>).

# Example 9: synthesis of synthesis of di-(2-(6-hydroxynaphthyl)anthracene (compound 9)

[0036] Starting material (35.0 g, 71.4 mmol), pyridine hydrochloride (72.0 g, 682 mmol), and 105 mL of phenyl ether-biphenyl eutectic were placed under nitrogen in a round bottomed flask equipped with a condenser. The reaction was refluxed for 2 days and then cooled slightly. Hexane was added to prevent the mixture from solidifying and the mixture was stirred for 30 minutes. The solid was collected by vacuum filtration. The solid product was added to an Erlenmeyer with ethanol and heated at 70 °C for 2 hours. After cooling, the solid was collected by filtration and dried in an oven to give pure product 28.5 g (86% yield). The product was sublimed prior to polymerization. Elemental analysis: calcd. for  $C_{34}H_{22}O_{2}$ : C 88.30%, H, 4.80%; found: C 88.02%, H 4.91%.

#### Example 10: synthesis of 2,6-di(2-ethylhexyloxy)anthraquinone (compound 10)

[0037] 2,6-Dihydroxyanthraquinone (100.0g, 0.42 mol) and 2-ethylhexyl bromide (165.0 g, 0.86 mol) were dissolved in 1 L of DMF. To this solution was added anhydrous  $K_2CO_3$  (120.0g. 0.87 mol). The reaction was heated at 90 °C overnight. Most of DMF was removed and 500 mL of water was added. The reaction was extracted with ether (3x400 mL), washed with brine (1x200 mL), and dried over MgSO<sub>4</sub>. Solvent was removed and the crude product was recrystallized from methanol to give yellow powdery product 125.2 g (65% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 0.92 - 0.98 (m, 12H, CH<sub>3</sub>), 1.34 - 1.54 (m, 16H), 1.75 - 1.81 (m, 2H, CH<sub>2</sub>(CH<sub>3</sub>)), 4.02 (d, J = 5.5 Hz, 4H, OCH<sub>2</sub>), 7.19 (d, J = 8.4 Hz, 2H), 7.70 (s, 2H), 8.19 (d, J = 8.5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 11.12, 14.06, 23.04, 23.88, 29.08, 30.51, 39.34, 71.34, 110.64, 120.84, 127.00, 129.62, 135.88, 164.29, 182.27. M.p. 49-51 °C; FD-MS: m/z 464 (M<sup>+</sup>).

# Example 11. synthesis of 2,6-di(2-ethylhexyloxy)anthracene (compound 11)

[0038] To a 1 L round bottom flask was added tin (80.0 g, 0.67 mol), 2,6-di(2-ethylhexyloxy)anthraquinone 10 (75.0 g, 0.16 mol), and 375 mL of acetic acid. The reaction was refluxed for 2 h during which the reaction became a slurry. The reaction was cooled to room temperature and the top layer was decanted. The solid was washed with  $CH_2Cl_2$ . The combined organic phase was washed with water, saturated NaHCO $_3$  solution, and brine and dried over MgSO $_4$ . Solvent was removed to yield 72.0 g of yellow solid. The yellow solid was dissolved in 200 mL of isopropanol and added dropwise to a solution of NaBH $_4$  (6.5 g, 0.17 mol) in 300 mL of isopropanol. The reaction was heated at reflux overnight. After cooled to room temperature, the reaction was quenched with dilute HCl solution and then poured into water. The yellow precipitate was collected by filtration, washed with water and ethanol and dried to give pure product was yellow powder 55.2 g (78% yield in two steps).  $^1$ H NMR (CDCl $_3$ )  $\delta$  (ppm): 0.92 - 1.62 (m, 14H, alkyl), 1.79-1.87 (m, 1 H, alkyl), 3.99 (d, J = 5.7 Hz, 2H, OCH $_2$ ), 7.14 (d, J = 9.4 Hz, 2H), 7.17 (s, 2H, 1 and 5 of anthracene), 8.17 (s, 2H, 9 and 10 of anthracene);  $^{13}$ C NMR (CDCl $_3$ ): 11.19, 14.10, 23.10, 24.07, 29.18, 30.72, 39.44, 70.48, 104.58, 120.85, 124.09, 128.71, 129.06, 131.30, 156.22. M.p. 60-62 °C; FD-MS: m/z 436 (M $^+$ ).

# Example 12: synthesis of 9,10-dibromo-2,6-di(2-ethylhexyloxy)anthracene (compound 12)

[0039] 2,6-Di(2-ethylhexyloxy)anthracene 11 (13.50 g, 0.031 mol) was added to 150 mL of DMF and cooled down to 0 °C. To this suspension was added NBS (11.60 g, 0.065 mol) in 60 mL of DMF. Upon the addition of NBS, the reaction became clear and turned to dark green color. The reaction was stirred at room temperature under nitrogen overnight. The reaction was poured into 200 mL of water, and extracted with methylene chloride (3x300 mL). The combined organic phase was washed thoroughly with water (3x100 mL) and brine (1x100 mL), and dried over MgSO<sub>4</sub>. After removal of the solvent, the dark brown residue was washed with hexane to collect greenish yellow crystals. The crude crystals were recrystallized from acetone to give flake like greenish yellow fluorescent product. The filtrates were combined and purified by chromatography on silica gel with hexane as eluent. Total yield: 5.5 g (30% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 0.93 - 1.70 (m, 14H, alkyl), 1.81 - 1.89 (m, 1 H, alkyl), 3.12 (d, J = 5.4 Hz, 2H, OCH<sub>2</sub>), 7.34 (d, J = 9.2Hz, 2H), 8.00 (d, J = 9.2 Hz, 2H), 8.71 (s, 2H, 1 and 5 of anthracene); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 11.12, 14.10, 23.08, 23.93, 29.15, 30.52, 39.88, 72.76, 107.74, 117.02, 125.27, 129.51, 129.75, 130.12, 152.87. M.p. 103-105 °C; FD-MS: m/z 590 (M<sup>+</sup>).

55

5

#### Synthesis of Polymers

10

15

30

40

### Example 13: synthesis of polymer 26

[0040] 2,2-Dimethyltrimethylene diboronate 3 (1.50 g, 2.0 mmol), 9,10-dibromoanthracene (0.68 g, 2.0 mmol), and Aliquat<sup>®</sup> 336 (0.11 g, 0.25 mmol) were dissolved in 8.6 mL of toluene. To this solution was added 2 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (3.3 mL, 6.6 mmol). The reaction mixture was bubbled with dry nitrogen for 15 min and catalyst tetrakis(triphenylphosphine)palladium (71 mg, 3mol%) was added. The reaction was heated under vigorous reflux for 24 h, and small amount of phenylboronic acid was added for end-capping of bromo group. The reaction was heated for 13 h and bromobenzene was added to end-cap boronate group. The reaction was heated for another 6 h and then poured into 200 mL of methanol. The precipitated polymer was washed with methanol, diluted HCI solution, and dried to give light yellow powdery polymer. The polymer was then extracted with acetone with a Sohxlet setup overnight to removed oligomer and residual catalyst. Polymer was re-precipitated from THF into methanol three times to give final polymer 1.00 g (71% yield).

### Example 14: synthesis of polymer 28

[0041] The procedure used to prepare polymer 26 was followed. 2,2-Dimethyltrimethylene diboronate 3 (1.50 g, 2.0 mmol), 9,10-dibromo-2,6/2,7-di(t-butyl)anthracene 7 (0.91 g, 2.0 mmol), and Aliquat<sup>®</sup> 336 (0.11 g, 0.25 mmol) were dissolved in 8.6 mL of toluene. To this solution were added 2 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (3.3 mL, 6.6 mmol) and palladium catalyst (71 mg, 3mol%). After polymerization and purification 1.15 g of off-white polymer was obtained.

### Example 15: synthesis of polymer 30

[0042] The procedure used to prepare polymer 26 was followed. 2,2-Dimethyltrimethylene diboronate 3 (1.50 g, 2.0 mmol), 9,10-dibromo-2,6-di(2-ethylhexyloxyl)anthracene 12 (1.21 g, 2.0 mmol), and Aliquat<sup>®</sup> 336 (0.11 g, 0.25 mmol) were dissolved in 8.6 mL of toluene. To this solution were added 2 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (3.3 mL, 6.6 mmol) and palladium catalyst (71 mg, 3mol%). After polymerization and purification polymer was obtained as greenish yellow solid.

#### Example 16: synthesis of polymer 47

[0043] Di-naphthanol 9 0.72 g (1.6 mmol) was dissolved in 12 mL of anhydrous pyridine and the mixture was cooled to 0 °C in an ice bath and stirred for 30 minutes. Di-acid chloride of 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1H-Indene-5-carboxylic acid (0.56 g, 1.6 mmol) was added as solid and the reaction was stirred at room temperature for 3 hours, during which time the reaction became very viscous and formed gel like solid. The reaction was poured into 100 mL of 10% HCl aqueous solution and the precipitated polymer was filtered, washed with water and methanol. The polymer was re-dissolved in 70:30 (v/v) of methylene chloride and hexafluoroisopropanol (HFIP) mixed solvent and precipitated into ethanol. The off-white polymer was collected and dried, yield 1.00 g (86%).

### Example 17: synthesis of polymer 8

[0044] The procedure used to prepare polymer 47 was followed. Di-naphthanol 9 (1.15 g, 2.5 mmol) reacted with dodecanedioyl dichloride (0.66 g, 2.5 mmol) in 16 mL of anhydrous pyridine to give 1.5 g of polymer as off-white solid (92% yield)

### Example 18: synthesis of polymer 89

[0045] The procedure used to prepare polymer 47 was followed. Di-naphthanol 9 (0.99 g, 2.1 mmol) reacted with 5-(octadecyloxy)isophthaloyl dichloride (1.02 g, 2.1 mmol) in 16 mL of anhydrous pyridine to give 1.6 g of polymer as off-white solid (87% yield).

# Example 19: synthesis of polymer 52

[0046] Di-naphthanol 9 (0.66 g, 1.4 mmol) was dissolved in 12 mL of anhydrous NMP and triethyamine (0.32 g, 3.2 mmol) was added. The mixture was cooled to 0 °C and stirred for 30 minutes. 4,4-(Hexafluoroisopropylidene)bis(benzoyl chloride) (0.61 g, 1.4 mmol) was added as solid. The reaction became viscous and was stirred at room temperature overnight. The mixture was poured into 150 mL of water. The precipitated polymer was filtered and re-dissolved in 3/7

HFIP/methylene chloride and precipitated into methanol. After two more precipitation, the polymer was collected and dried as off-white solid, yield 1.00 g (88%).

#### Example 20: synthesis of polymer 44

[0047] The procedure used to prepare polymer 52 was followed. Di-naphthanol 9 (1.00 g, 2.2 mmol) reacted with bisphenol A bis(chloroformate) (0.78 g, 2.2 mmol) in 20 mL of anhydrous NMP in the presence of triethylamine (0.48 g, 0.47 mmol) to give 1.3 g of polymer as off-white solid (90% yield).

#### EL Device Fabrication and Performance

#### Example 21

5

15

20

25

35

40

45

50

55

[0048] An EL device satisfying the requirements of the invention was constructed in the following manner. The organic EL medium has single layer of polymer thin film.

- (a) An indium-tin-oxide (ITO) coated glass substrate was sequentially ultra-sonicated in a commercial detergent, rinsed with deionized water, degreased in toluene vapor and exposed to ultraviolet light and ozone for a few minutes.
- (b) A polymer solution (30 mg in 30 mL of solvent) was filtered through a 2 μm PTFE filter. The polymer solution was then spin-coated onto ITO under a controlled spinning speed. The thickness of the polymer film was between 500-700 Angstroms.
- (c) On top of the polymer film was deposited a cathode layer 2000 Angstroms thick consisting of a 10:1 atomic ratio of Mg and Ag.

[0049] The above sequence completed the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

[0050] The blue light output from EL device was about 50 cd/m<sup>2</sup> at about 10 V.

[0051] Table 1 summarizes the characterization of the polymers prepared in the present invention. Polymers have reasonable molecular weights and show high onset thermal decomposition temperature  $T_d$ . UV and photoluminescence (PL) spectra were obtained from dilute solutions and solid thin films of the polymers and EL spectra were obtained from ITO/polymer/Mg:Ag EL devices. The fabrication of EL devices was illustrated in example 21. FIGS. 4 and 5 show the UV, PL and El spectra of polymers 26 and 28 respectively. The voltage-current characteristics of the EL device of polymer 28 is shown in FIG 6.

Table 1

Characterization of polymers according to Examples.						
Polymer	M <sub>w</sub>	T <sub>d</sub> (°C)	T <sub>g</sub> (°C)	UV (λ <sub>max</sub> nm)	PL (λ <sub>max</sub> nm)	EL (λ <sub>max</sub> nm)
26	9,680 <sup>a</sup>	353	86	379	441	468
28	10,000 <sup>a</sup>	412	112	379	449	468
30	17,600 <sup>a</sup>	390	46	416	464 <sup>d</sup>	
8	10,800 <sup>b</sup>	400	98	378	449	
44	9,270 <sup>b</sup>	425	137	378	448	
47	27,400 <sup>b</sup>	428	NO <sup>c</sup>	378	448	
52	23,900 <sup>b</sup>	500	232	378	448	
89	52,800 <sup>b</sup>	415	135	379	448	

<sup>&</sup>lt;sup>a</sup> weight average molecular weight, determined by size exclusion chromatography in THF using polystyrene standard.

b weight average molecular weight, determined by size exclusion chromatography in 20/80 dichloroacetic acid/dichloromethane containing 0.01 M tetrabutylammonium acetate using polystyrene standard.

c not observed

d excited at 400 run, the rest of polymer films were excited at 370 nm; both UV and PL are measured in dilute toluene solution.

[0052] Other features of the invention are included below.

[0053] The electroluminescent device wherein Y are aryl groups having the following structures connected by a linking group Z

5 wherein:

 $Ar_1$  and  $Ar_2$  are substituted or unsubstituted aromatic groups containing 6 to 28 carbon atoms, Z is a divalent linking groups containing 0 to 12 carbon atoms.

[0054] The electroluminescent device wherein Z contains N, Si, O, Cl, F, Br, or S atoms.

[0055] The electroluminescent device wherein Y are aryl hydrocarbons:

(Ar)

wherein:

15

20

25

30

35

40

45

50

55

Ar is substituted or unsubstituted aryl groups with 6 to 28 carbon atoms.

[0056] An electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracene-based polymers of the following formula:

 $R_3$   $R_4$  X-Y-X  $R_3$ 

wherein:

R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are each individually hydrogen, or alkyl, or alkoxy of from 1 to 24 carbon atoms; aryl or substituted aryl of from 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl of from 4 to 40 carbons; or F, Cl, or Br; or a cyano group; or a nitro group.

X includes a linking group of one or more carbon-carbon, ether or thioether, or ester anhydride, carbonate, sulfonyl, or sulfinyl, amine, amide, or urea; and

Y includes one or more comonomer units that are a substituted or unsubstituted alkyl, aryl, heteroaryl, or a conjugated group.

[0057] The electroluminescent device wherein the carbon-carbon linking group includes:

10 15

wherein R is hydrogen, or alkyl group containing 1 to 24 carbon atoms; aryl or substituted aryl of containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons; or F, Cl, or Br, or a cyano group. [0058] The electroluminescent device wherein the ester linking group includes:

[0059] The electroluminescent device wherein the anhydride linking group includes: 35

[0060] The electroluminescent device wherein the carbonate linking group includes:

$$-0$$

[0061] The electroluminescent device wherein the sulfonyl or sulfinyl linking group includes:

55

5

20

30

40

[0062] The electroluminescent device wherein the amine linking group includes:

wherein R is hydrogen, or alkyl group containing 1 to 24 carbon atoms; aryl or substituted aryl of containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons.

[0063] The electroluminescent device wherein the amide linking group includes:

$$\begin{array}{ccc} R & O \\ -N-C-; \text{ or } \end{array}$$

wherein R is hydrogen, or alkyl group containing 1 to 24 carbon atoms; aryl or substituted aryl of containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons.

[0064] The electroluminescent device wherein the urea linking group includes:

wherein R is hydrogen, or alkyl group containing 1 to 24 carbon atoms; aryl or substituted aryl of containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons.

[0065] The electroluminescent device wherein the aryl linking group includes

(Ar)<sub>n</sub>

wherein Ar is an aryl or substituted aryl group of containing 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl containing 4 to 40 carbons; n is an integer of from 1 to 6.

## **PARTS LIST**

[0066]

5

10

20

25

30

35

40

50

55

10 substrate

	30	hole transport layer
	40	electron transport layer
	50	electroluminescent medium
	60	cathode
5	100	substrate
	200	anode
	300	hole transport layer
	400	emissive layer
	500	electron transport layer
10	600	electroluminescent medium
	700	cathode
	1000	substrate
	2000	anode
	3000	emitting layer
15	4000	cathode

#### Claims

20

25

30

35

40

1. An electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracenebased polymers of the following formula:

$$\begin{array}{c|c}
 & R_1 \\
 & R_2 \\
 & R_3
\end{array}$$

wherein:

R,  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are each individually hydrogen, or alkyl, or alkoxy of from 1 to 24 carbon atoms; aryl or substituted aryl of from 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl of from 4 to 40 carbons; or R, R, R, or R, or a cyano group; or a nitro group;

X is a linking group; and

Y includes one or more comonomer units that are a substituted or unsubstituted alkyl, alkenyl, aryl, or heteroaryl or a conjugated group.

- 2. The electroluminescent device of claim 1 wherein when Y is alkyl it includes from 1 to 24 carbon atoms.
- 45 3. The electroluminescent device of claim 2 further including N,S,F,Cl, Br or Si atoms.
  - 4. The electroluminescent device of claim 1 wherein Y are alkyl groups having the following structures:

 $R_1$ =2-ethylhexyloxy,  $R_2$ =H, m=6  $R_1$ =n-hexyl,  $R_2$ =n-hexyloxy, m=4  $R_1$ =t-butyl,  $R_2$ =n-hexyloxy, m=6;

5

10

15

20

*2*5

30

40

45

50

 $R_1$ =2-ethylhexyloxy,  $R_2$ =H, m=6  $R_1$ =n-hexyl,  $R_2$ =n-hexyloxy, m=4  $R_1$ =t-butyl,  $R_2$ =n-hexyloxy, m=6  $R_1$ = $R_2$ =n-hexyl, m=8  $R_1$ = $R_2$ =H, m=12;

 $R_1$ =H,  $R_2$ =2-ethylhexyloxy, p=4, q=3  $R_1$ =n-hexyl,  $R_2$ =t-butyl, p=4, q=3  $R_1$ =n-hexyl,  $R_2$ =t-butyl, p=4, q=5;

$$R_1$$
 $R_2$ 
 $R_2$ 
 $R_1$ 
 $R_2$ 
 $R_2$ 
 $R_1$ 
 $R_2$ 
 $R_2$ 
 $R_3$ 
 $R_4$ 
 $R_4$ 
 $R_5$ 
 $R_7$ 
 $R_7$ 

 $R_1$ =H,  $R_2$ =2-ethylhexyloxy, X=O, p=6  $R_1$ =n-hexyl,  $R_2$ =2-ethylhexyloxy, X=O, p=4  $R_1$ =2-ethylhexyl,  $R_2$ =t-butyl, X=S, p=4  $R_1$ =n-hexyoxy,  $R_2$ =t-butyl, X=S, p=4;

 $R_1=H$ ,  $R_2=2$ -ethylhexyloxy, p=6 15 R<sub>1</sub>=n-hexyl, R<sub>2</sub>=2-ethylhexyloxy, p=4 R<sub>1</sub>=2-ethylhexyl, R<sub>2</sub>=t-butyl, p=4  $R_1$ =2-ethylhexyloxy,  $R_2$ =H, p=4;

$$\begin{array}{c} R_1 \\ R_2 \\ N-(CH_2)p-N-(CH_2)p-N \\ \end{array}$$

30  $R_1$ =2-ethylhexyloxy,  $R_2$ =H, p=4, q=3 R<sub>1</sub>=t-butyl, R<sub>2</sub>=2-ethylhexyl, p=4, q=5  $R_1$ =n-hexyl,  $R_2$ =2-ethylhexyloxy, p=4, q=5;

$$R_1$$
 $R_2$ 
 $R_2$ 
 $R_2$ 
 $R_1$ 
 $R_2$ 
 $R_2$ 
 $R_1$ 

 $R_1$ =2-ethylhexyloxy,  $R_2$ =H, m=8 R<sub>1</sub>=t-butyl, R<sub>2</sub>=2-ethylhexyl, m=4  $R_1$ =n-hexyl,  $R_2$ =2-ethylhexyloxy, m=2; or

55

5

20

25

35

40

45

 $R_1=R_2=H$ , m=11  $R_1=t$ -butyl,  $R_2=2$ -ethylhexyl, m=7  $R_1=t$ -butyl,  $R_2=H$ , m=11  $R_1=n$ -hexyl,  $R_2=2$ -ethylhexyloxy, m=5  $R_1=2$ -ethylhexyloxy,  $R_2=H$ , m=11.

10

25

30

35

40

45

50

20 5. An electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracenebased polymers having the following formulas:

$$R_1$$
 $R_2$ 
 $C=C$ 
 $R_3$ 
 $C=C$ 
 $R_3$ 
 $C=C$ 

 $\begin{array}{l} {\rm R_{1}=2\text{-}ethylhexyloxy,\ R_{2}=R_{3}=H,\ p=6} \\ {\rm R_{1}=R_{3}=H,\ R_{2}=2\text{-}ethylhexyloxy,\ p=12} \\ {\rm R_{1}=n\text{-}hexyl,\ R_{2}=R_{3}=H,\ p=12} \\ {\rm R_{1}=t\text{-}butyl,\ R_{2}=R_{3}=n\text{-}hexyl,\ p=6;} \end{array}$ 

 $\begin{array}{c} R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_3 = H, \ R_4 = CH_3, \ X = C \\ R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_3 = H, \ R_4 = CF_3, \ X = C \\ S_5 \\ R_1 = t\text{-butyl}, \ R_2 = 2\text{-ethylhexyloxy}, \ R_3 = H, \ R_4 = CF_3, \ X = C \\ R_1 = t\text{-butyl}, \ R_2 = n\text{-hexyloxy}, \ R_3 = H, \ R_4 = CF_3, \ X = Si \\ R_1 = t\text{-butyl}, \ R_2 = 2\text{-ethylhexyloxy}, \ R_3 = H, \ R_4 = CF_3, \ X = Si \\ R_1 = H, \ R_2 = 2\text{-ethylhexyloxy}, \ R_3 = H, \ R_4 = CF_3, \ X = Si \\ \end{array}$ 

 $\begin{array}{l} R_1 = 2 \text{-ethylhexyloxy}, \ R_2 = R_3 = H, \ R_4 = \text{CH}_3, \ X = \text{C} \\ R_1 = 2 \text{-ethylhexyloxy}, \ R_2 = R_3 = H, \ R_4 = \text{CF}_3, \ X = \text{C} \\ R_1 = 1 \text{-butyl}, \ R_2 = 2 \text{-ethylhexyloxy}, \ R_3 = H, \ R_4 = \text{CF}_3, \ X = \text{Si} \\ R_1 = R_2 = R_3 = H, \ R_4 = \text{CH}_3, \ X = \text{C} \\ \text{polyR}_1 = H, \ R_2 = 2 \text{-ethylhexyloxy}, \ R_3 = H, \ R_4 = \text{CF}_3, \ X = \text{Si}; \end{array}$ 

$$\begin{split} &R_1\text{=}2\text{-ethylhexyloxy},\ R_2\text{=}H,\ R_3\text{=}R_4\text{=}CH_3\\ &R_1\text{=}R_2\text{=}H,\ R_3\text{=}R_4\text{=}CH_3\\ &R_1\text{=}H,\ R_2\text{=}2\text{-ethylhexyloxy},\ R_3\text{=}n\text{-butyl},\ R_4\text{=}CH_3 \end{split}$$

 $R_1 = 2\text{-ethylhexyloxy}, \ R_2 = H, \ R_3 = CH_3, \ R_4 = H, \ X = C$   $R_1 = t\text{-butyl}, \ R_2 = n\text{-hexyloxy}, \ R_3 = CH_3, \ R_4 = H, \ X = C$   $R_1 = t\text{-butyl}, \ R_2 = n\text{-hexyloxy}, \ R_3 = n\text{-butyl}, \ R_4 = H, \ X = Si$   $R_1 = R_2 = R_4 = H, \ R_3 = CF_3, \ X = C$   $R_1 = H, \ R_2 = 2\text{-ethylhexyloxy}, \ R_3 = CH_3, \ R_4 = n\text{-butyl}, \ X = Si;$ 

 $R_1$ =2-ethylhexyloxy,  $R_2$ =n-butyl,  $R_3$ =phenyl  $R_1$ =t-butyl,  $R_2$ =n-hexyloxy,  $R_3$ =phenyl poly $R_1$ =2-ethylhexyloxy,  $R_2$ =H,  $R_3$ =n-butyl  $R_1$ =n-hexyl,  $R_2$ =2-ethylhexyloxy,  $R_3$ =phenyl;

$$\begin{bmatrix} R_1 & R_2 & 0 & R_3 \\ N - C - N & N - C - N \end{bmatrix}$$

$$\begin{split} &R_1\text{=}2\text{-}ethylhexyloxy, \ R_2\text{=}H, \ R_3\text{=}n\text{-}hexyl} \\ &R_1\text{=}2\text{-}ethylhexyloxy, \ R_2\text{=}H, \ R_3\text{=}n\text{-}hexyl} \\ &R_1\text{=}2\text{-}ethylhexyloxy, \ R_2\text{=}H, \ R_3\text{=}n\text{-}hexyl} \\ &R_1\text{=}t\text{-}butyl, \ R_2\text{=}H, \ R_3\text{=}2\text{-}ethylhexyl} \\ &R_1\text{=}H, \ R_2\text{=}n\text{-}hexyloxy, \ R_3\text{=}n\text{-}hexyl} \\ &R_1\text{=}2\text{-}ethylnexyloxy, \ R_2\text{=}H, \ R_3\text{=}4\text{-}methyloxyphenyl}; \end{split}$$

$$\begin{array}{c|c}
R_1 \\
R_2 \\
R_1
\end{array}$$

$$\begin{array}{c|c}
R_2 \\
R_1
\end{array}$$

 $\begin{array}{lll} \text{50} & \text{R}_1\text{=2-ethylhexyloxy, R}_2\text{=H, X=O} \\ & \text{R}_1\text{=2-ethylhexyloxy, R}_2\text{=H, X=S} \\ & \text{R}_1\text{=t-butyl, R}_2\text{=n-hexyloxy, X=O} \\ & \text{R}_1\text{=2-ethylhexyloxy, R}_2\text{=n-hexyl, X=O;} \end{array}$ 

5

 $R_1$ =2-ethylhexyloxy,  $R_2$ =H,  $R_3$ = $R_4$ =n-hexyl  $R_1$ =n-hexyl,  $R_2$ =H,  $R_3$ = $R_4$ =n-hexyl  $R_1$ = -butyl,  $R_2$ =n-hexyl,  $R_3$ = $R_4$ =4-methyloxyphenyl  $R_1$ = $R_2$ =n-hexyloxy,  $R_3$ = $R_4$ =n-hexyl;

$$\begin{bmatrix} R_1 \\ R_2 \\ R_1 \end{bmatrix}$$

 $R_1$ =2-ethylhexyloxy,  $R_2$ =H  $R_1$ =t-butyl,  $R_2$ =n-hexyloxy  $R_1$ = $R_2$ =n-hexyl  $R_1$ =2-ethylhexyloxy,  $R_2$ =t-butyl;

 $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ =H  $R_1$ = $R_2$ =n-hexyl,  $R_3$ =H  $R_1$ =t-butyl,  $R_2$ =n-hexyloxy,  $R_3$ =H $R_1$ =t-butyl,  $R_2$ = $R_3$ =n-hexyloxy; or

55

5

10

15

20

25

30

35

40

15  $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ =H  $R_1$ =t-butyl,  $R_2$ =n-hexyl,  $R_3$ =n-hexyloxy  $R_1$ =t-butyl,  $R_2$ =n-hexyloxy,  $R_3$ =H  $R_1$ =2-ethylhexyloxy,  $R_2$ =H,  $R_3$ =n-hexyloxy.

25

30

35

45

50

20 6. An electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracenebased polymers having the following formulas:

$$\begin{bmatrix} R_1 \\ R_2 \\ R_1 \end{bmatrix}$$

 $\begin{array}{ll} & R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_3 = H, \ p = 0 \\ & R_1 = R_2 = n\text{-hexyl}, \ R_3 = H, \ p = 1 \\ & 40 & R_1 = t\text{-butyl}, \ R_2 = n\text{-hexyloxy}, \ R_3 = H, \ p = 2 \\ & R_1 = t\text{-butyl}, \ R_2 = R_3 = n\text{-hexyloxy}, \ p = 1 \end{array}$ 

 $R_1$ =2-ethylhexyloxy,  $R_2$ =H, m=5  $R_1$ =n-hexyl,  $R_2$ =H, m=17  $R_1$ =t-butyl,  $R_2$ =n-hexyloxy, m=7  $R_1$ =t-butyl,  $R_2$ = $R_3$ =n-hexyloxy, m=9

$$\begin{bmatrix} R_1 \\ C \\ R_2 \end{bmatrix} = \begin{bmatrix} R_2 \\ C \\ R_3 \end{bmatrix} \begin{bmatrix} R_3 \\ C \\ C \end{bmatrix}$$

$$\begin{split} &R_1\text{=}2\text{-ethylhexyloxy},\ R_2\text{=}R_3\text{=}H\\ &R_1\text{=}R_2\text{=}n\text{-hexyl},\ R_3\text{=}H\\ &R_1\text{=}t\text{-butyl},\ R_2\text{=}R_3\text{=}n\text{-hexyloxy}\\ &R_1\text{=}t\text{-butyl},\ R_2\text{=}n\text{-hexyloxy},\ R_3\text{=}H \end{split}$$

 $\begin{array}{l} R_1 = \text{t-butyl}, \ R_2 = \text{n-hexyloxy}, \ R_3 = R_4 = H \\ R_1 = 2 - \text{ethylhexyl}, \ R_2 = R_4 = H, \ R_3 = \text{n-hexyloxy} \\ R_1 = 2 - \text{ethylhexyloxy}, \ R_2 = R_3 = \text{n-hexyloxy}, \ R_4 = H \\ R_1 = \text{n-hexyl}, \ R_2 = R_3 = \text{n-hexyloxy}, \ R_3 = R_4 = H \end{array}$ 

 $\rm R_1=t$ -butyl,  $\rm R_2=n$ -hexyloxy,  $\rm R_3=R_4=H,$   $\rm p=q=1$   $\rm R_1=2$ -ethylhexyl,  $\rm R_2=R_4=H,$   $\rm R_3=n$ -hexyloxy,  $\rm p=q=1$   $\rm R_1=2$ -ethylhexyloxy,  $\rm R_2=R_3=n$ -hexyloxy,  $\rm R_4=H,$   $\rm p=q=2$   $\rm R_1=n$ -hexyl,  $\rm R_2=R_3=n$ -hexyloxy,  $\rm R_4=H,$   $\rm p=q=2$   $\rm R_1=2$ -ethylhexyloxy,  $\rm R_2=R_3=H,$   $\rm R_4=n$ -hexyl,  $\rm p=q=2$   $\rm R_1=n$ -hexyl,  $\rm R_2=R_4=n$ -hexyloxy,  $\rm R_3=H,$   $\rm p=q=2$ 

$$\begin{split} &R_1\text{=}\text{t-butyl}, \ R_2\text{=}\text{n-hexyloxy}, \ R_3\text{=}R_4\text{=}\text{H} \\ &R_1\text{=}2\text{-}\text{ethylhexyl}, \ R_2\text{=}R_4\text{=}\text{H}, \ R_3\text{=}\text{n-hexyloxy} \\ &R_1\text{=}2\text{-}\text{ethylhexyloxy}, \ R_2\text{=}R_3\text{=}\text{n-hexyloxy}, \ R_4\text{=}\text{H} \\ &R_1\text{=}\text{n-hexyl}, \ R_2\text{=}R_3\text{=}\text{n-hexyloxy}, \ R_3\text{=}R_4\text{=}\text{H} \end{split}$$

 $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ =H  $R_1$ = $R_2$ =n-hexyl,  $R_3$ =H  $R_1$ =t-butyl,  $R_2$ = $R_3$ =n-hexyloxy  $R_1$ =2-ethylhexyloxy,  $R_2$ =H,  $R_3$ =n-hexyloxy

 $\begin{array}{lll} \it{50} & R_1=2\text{-ethylhexyloxy}, \ R_2=R_3=H \\ R_1=2\text{-ethylhexyloxy}, \ R_2=n\text{-hexyl}, \ R_3=H \\ R_1=t\text{-butyl}, \ R_2=R_3=n\text{-hexyl} \end{array}$ 

55

5

10

15

20

25

30

35

40

 $\begin{array}{ll} {}^{15} & {\rm R_{1}=2\text{-}ethylhexyloxy, R_{2}=R_{3}=H} \\ {\rm R_{1}=2\text{-}ethylhexyloxy, R_{2}=n\text{-}hexyl, R_{3}=H} \\ {\rm R_{1}=t\text{-}butyl, R_{2}=R_{3}=n\text{-}hexyl} \\ {\rm R_{1}=2\text{-}ethylhexyloxy, R_{2}=H, R_{3}=n\text{-}hexyl} \end{array}$ 

20

25

30

35

40

45

 $\begin{bmatrix} R_1 & R_2 & 0 \\ R_2 & R_1 & C \end{bmatrix}$ 

 $R_1$ =2-ethylhexyloxy,  $R_2$ =n-hexyl,  $R_3$ =H  $R_1$ = $R_2$ = $R_3$ =n-hexyl  $R_1$ = $R_3$ =2-ethylhexyloxy,  $R_2$ =H

 $R_{1}$ =2-ethylhexyloxy,  $R_{2}$ =n-hexyl,  $R_{3}$ =H  $R_{1}$ = $R_{2}$ = $R_{3}$ =n-hexyl  $R_{1}$ = $R_{3}$ =2-ethylhexyloxy,  $R_{2}$ =H  $R_{1}$ =2-ethylhexyloxy,  $R_{2}$ = $R_{3}$ =H

7. An electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracene-based polymers of the following formula:

wherein:

5

10

15

20

25

40

45

50

55

 $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are each individually hydrogen, or alkyl, or alkoxy of from 1 to 24 carbon atoms; aryl or substituted aryl of from 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl of from 4 to 40 carbons; or  $F_1$ ,  $F_2$ ,  $F_3$ , or  $F_4$ , or  $F_5$ , or a cyano group; or a nitro group.

X is a linking group; and

Y includes the following formula

$$-Ar_1$$
 $R'$ 
 $R'$ 

30 wherein:

 ${\rm Ar}_1$  and  ${\rm Ar}_2$  are substituted or unsubstituted aryl groups with 6 to 28 carbon atoms;

R' and R" are hydrogen, or alkyl group containing 1 to 12 carbon atoms, or Cl, Br, or F, or a cyano group; and p is an integer from 1 to 3.

8. An electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracenebased polymers having the following formulas:

 $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ = $R_4$ = $R_5$ =H

 $R_1=2$ -ethylhexyloxy,  $R_2=n$ -hexyl,  $R_3=R_4=R_5=H$ 

 $R_1$ =t-butyl,  $R_2$ =n-hexyl,  $R_3$ = $R_5$ =H,  $R_4$ =n-hexyloxy

R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>4</sub>=R<sub>5</sub>=H, R<sub>3</sub>=CN

 $R_1$ =2-ethylhexyloxy,  $R_2$ =n-hexyl,  $R_3$ =CN,  $R_4$ = $R_5$ =H;

$$\begin{bmatrix} R_1 & R_2 & R_3 & R_4 & R_5 & R_5 & R_4 & R_5 & R_5 & R_6 & R_5 & R_6 & R_$$

 $\begin{array}{ll} {\it 15} & {\it R}_1{=}2{\text{-ethylhexyloxy}}, \, {\it R}_2{=}R_3{=}R_4{=}R_5{=}H \\ {\it R}_1{=}2{\text{-ethylhexyloxy}}, \, {\it R}_2{=}n{\text{-hexyl}}, \, {\it R}_3{=}R_4{=}R_5{=}H \\ {\it R}_1{=}t{\text{-butyl}}, \, {\it R}_2{=}n{\text{-hexyl}}, \, {\it R}_3{=}R_5{=}H, \, {\it R}_4{=}n{\text{-hexyloxy}} \\ {\it R}_1{=}2{\text{-ethylhexyloxy}}, \, {\it R}_2{=}R_4{=}R_5{=}H, \, {\it R}_3{=}CN \\ {\it R}_1{=}2{\text{-ethylhexyloxy}}, \, {\it R}_2{=}n{\text{-hexyl}}, \, {\it R}_3{=}CN, \, {\it R}_4{=}R_5{=}H; \end{array}$ 

 $\begin{array}{l} R_1 = 2 \text{-ethylhexyloxy}, \ R_2 = R_3 = R_4 = R_5 = H \\ R_1 = 2 \text{-ethylhexyloxy}, \ R_2 = n \text{-hexyl}, \ R_3 = R_4 = R_5 = H \\ R_1 = t \text{-butyl}, \ R_2 = n \text{-hexyl}, \ R_3 = R_5 = H, \ R_4 = n \text{-hexyloxy} \\ R_1 = 2 \text{-ethylhexyloxy}, \ R_2 = R_4 = R_5 = H, \ R_3 = CN \\ R_1 = 2 \text{-ethylhexyloxy}, \ R_2 = n \text{-hexyl}, \ R_3 = CN, \ R_4 = R_5 = H; \end{array}$ 

$$\begin{bmatrix} R_1 & R_2 & R_5 & R_4 \\ \vdots & \vdots & \vdots & \vdots \\ R_2 & R_4 & \vdots \\ R_2 & R_4 & \vdots \\ \end{bmatrix}_{n}$$

 $\begin{array}{c} R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_3 = R_4 = R_5 = H \\ R_1 = 2\text{-ethylhexyloxy}, \ R_2 = n\text{-hexyl}, \ R_3 = R_4 = R_5 = H \\ R_1 = t\text{-butyl}, \ R_2 = n\text{-hexyl}, \ R_3 = R_5 = H, \ R_4 = n\text{-hexyloxy} \\ R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_4 = R_5 = H, \ R_3 = CN \\ R_1 = 2\text{-ethylhexyloxy}, \ R_2 = n\text{-hexyl}, \ R_3 = CN, \ R_4 = R_5 = H; \end{array}$ 

 $\begin{array}{l} R_1 = & 2\text{-ethylhexyloxy}, \ R_2 = R_3 = R_4 = R_5 = H, \ p = q = r = 1 \\ R_1 = & 2\text{-ethylhexyloxy}, \ R_2 = & n\text{-hexyl}, \ R_3 = R_4 = R_5 = H, \ p = q = r = 1 \\ R_1 = & 2\text{-ethylhexyloxy}, \ R_2 = & R_4 = R_5 = H, \ R_4 = & n\text{-hexyloxy}, \ p = q = r = 2 \\ R_1 = & 2\text{-ethylhexyloxy}, \ R_2 = & R_4 = R_5 = H, \ R_3 = & CN, \ p = q = r = 1 \\ R_1 = & 2\text{-ethylhexyloxy}, \ R_2 = & n\text{-hexyl}, \ R_3 = & CN, \ R_4 = & R_5 = H, \ p = q = r = 2; \ \text{or} \end{array}$ 

$$\begin{array}{c|c}
 & R_1 & R_2 & R_3 & R_4 & R_5 & R_5 & R_4 & R_5 & R_5 & R_6 &$$

 $\begin{array}{l} {\rm R_{1}=2\text{-}ethylhexyloxy,} \ \, {\rm R_{2}=R_{3}=R_{4}=R_{5}=H,} \ \, {\rm p=q=r=1} \\ {\rm R_{1}=2\text{-}ethylhexyloxy,} \ \, {\rm R_{2}=n\text{-}hexyl,} \ \, {\rm R_{3}=R_{5}=H,} \ \, {\rm R_{4}=R_{5}=H,} \ \, {\rm p=q=r=1} \\ {\rm R_{1}=2\text{-}ethylhexyloxy,} \ \, {\rm R_{2}=R_{4}=R_{5}=H,} \ \, {\rm R_{3}=CN,} \ \, {\rm p=q=r=1} \\ {\rm R_{1}=2\text{-}ethylhexyloxy,} \ \, {\rm R_{2}=n\text{-}hexyl,} \ \, {\rm R_{3}=CN,} \ \, {\rm R_{4}=R_{5}=H,} \ \, {\rm p=q=r=2.} \\ \end{array}$ 

9. An electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracenebased polymers of the following formula:

$$R_1$$
 $R_2$ 
 $R_3$ 
 $R_2$ 
 $R_3$ 

wherein:

5

10

15

20

25

30

35

40

45

50

R,  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are each individually hydrogen, or alkyl, or alkoxy of from 1 to 24 carbon atoms; aryl or substituted aryl of from 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl of from 4 to 40 carbons; or F, Cl, or Br; or a cyano group; or a nitro group.

X is a linking group; and

5

10

15

20

25

30

35

40

45

50

55

Y includes substituted or unsubstituted heteroaryl groups having from 4 to 40 carbon atoms and at least one or more of N, S, or O atoms.

10. An electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracenebased polymers having the following formulas:

$$\begin{array}{c|c}
R_1 & R_2 \\
R_2 & R_3
\end{array}$$

R<sub>1</sub>=2-ethylhexyloxy, R<sub>2</sub>=R<sub>3</sub>=H, p=1

 $R_1$ =2-ethylhexyloxy,  $R_2$ = $R_3$ =H, p=2

 $R_1$ =2-ethylhexyloxy,  $R_2$ =H,  $R_3$ =n-hexyl, p=1

 $R_1$ =t-butyl,  $R_2$ =n-hexyloxy,  $R_3$ =H, p=1;

 $\begin{array}{l} R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_3 = H, \ R_4 = n\text{-hexyl}, \ p = 1 \\ R_1 = t\text{-butyl}, \ R_2 = n\text{-hexyl}, \ R_3 = H, \ R_4 \text{-ethylhexyl}, \ p = 2 \\ R_1 = 2\text{-ethylhexyloxy}, \ R_2 = H, \ R_3 = n\text{-hexyl}, \ R_4 = 2\text{-ethylhexyl}, \ p = 2 \\ R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_3 = n\text{-hexyl}, \ R_4 = 2\text{-ethylhexyl}, \ p = 3; \end{array}$ 

$$\begin{bmatrix} R_1 & R_2 & Q & R_4 & R_3 & Q \\ C & Q & Q & Q & Q & Q \\ R_2 & R_2 & R_3 & Q & Q & Q \\ R_3 & R_4 & R_3 & Q & Q & Q \\ R_4 & R_5 & Q & Q & Q & Q \\ R_5 & Q & Q & Q & Q & Q \\ R_6 & Q & Q & Q & Q & Q & Q \\ R_7 & Q & Q & Q & Q & Q & Q \\ R_8 & Q & Q & Q & Q & Q & Q \\ R_9 & Q & Q & Q & Q & Q \\ R_9 & Q & Q & Q & Q & Q \\ R_9 & Q & Q & Q & Q & Q \\ R_9 & Q & Q & Q & Q & Q \\ R_9 & Q & Q & Q & Q & Q \\ R_9 & Q & Q & Q & Q & Q \\ R_9 & Q & Q & Q \\ R_9 & Q & Q & Q & Q \\ R_9 & Q & Q & Q \\ R_9 & Q & Q$$

$$\begin{split} &R_{1}\text{=}2\text{-ethylhexyloxy},\ R_{2}\text{=}R_{3}\text{=}R_{4}\text{=}H,\ p\text{=}\text{r=}0,\ q\text{=}1\\ &R_{1}\text{=}\text{t-butyl},\ R_{2}\text{=}\text{n-hexyl},\ R_{3}\text{=}R_{4}\text{=}2\text{-ethylhexyl},\ p\text{=}\text{r=}1,\ q\text{=}2\\ &R_{1}\text{=}R_{4}\text{=}2\text{-ethylhexyloxy},\ R_{2}\text{=}R_{3}\text{=}H,\ p\text{=}\text{r=}1\\ &R_{1}\text{=}R_{2}\text{=}2\text{-ethylhexyloxy},\ R_{3}\text{=}R_{4}\text{=}H,\ p\text{=}\text{r=}1,\ q\text{=}2\\ &R_{1}\text{=}\text{t-butyl},\ R_{2}\text{=}R_{3}\text{=}2\text{-ethylhexyloxy},\ R_{4}\text{=}H,\ p\text{=}\text{r=}1,\ q\text{=}2; \end{split}$$

 $\begin{array}{l} R_1 = 2 - e thylhexyloxy, \ R_2 = H_1, \ p = q = 1, \ X = O \\ R_1 = 2 - e thylhexyloxy, \ R_2 = H_1, \ p = q = 1, \ X = S \\ R_1 = 2 - e thylhexyloxy, \ R_2 = H_1, \ p = q = 1, \ X = n - h e x y l \\ R_1 = 2 - e thylhexyloxy, \ R_2 = n - h e x y l, \ p = q = 2, \ X = O \\ R_1 = 2 - e thylhexyloxy, \ R_2 = n - h e x y l, \ p = q = 2, \ X = N - h e x y l; \\ R_1 = 2 - e thylhexyloxy, \ R_2 = n - h e x y l, \ p = q = 2, \ X = N - h e x y l; \\ \end{array}$ 

$$\begin{bmatrix} R_1 & R_2 & R_3 & N & O & N-C \\ R_2 & R_1 & R_3 & N & O & N-C \\ R_2 & R_1 & R_3 & R_3 & R_3 & R_3 \end{bmatrix}$$

$$\begin{split} &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_3 = H \\ &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = H, \ R_3 = \text{phenyl} \\ &R_1 = t\text{-butyl}, \ R_2 = R_3 = n\text{-hexyl} \\ &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = H, \ R_3 = n\text{-hexyloxy} \\ &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = n\text{-hexyloxy}, R_3 = H; \end{split}$$

 $\begin{aligned} &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_3 = H \\ &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = H, \ R_3 = \text{phenyl} \\ &R_1 = t\text{-butyl}, \ R_2 = R_3 = n\text{-hexyl} \end{aligned}$ 

5

10

15

20

25

30

35

40

45

50

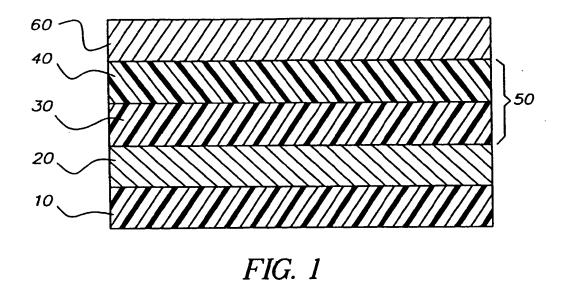
 $R_1$ =2-ethylhexyloxy,  $R_2$ =H,  $R_3$ =n-hexyloxy

 $R_1$ =2-ethylhexyloxy,  $R_2$ =n-hexyloxy,  $R_3$ =H;

$$\begin{split} &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_3 = H \\ &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = H, \ R_3 = \text{phenyl} \\ &R_1 = t\text{-butyl}, \ R_2 = R_3 = n\text{-hexyl} \\ &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = H, \ R_3 = n\text{-hexyl}; \end{split}$$

$$\begin{split} &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = R_3 = H \\ &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = H, \ R_3 = \text{phenyl} \\ &R_1 = t\text{-butyl}, \ R_2 = R_3 = n\text{-hexyl} \\ &R_1 = 2\text{-ethylhexyloxy}, \ R_2 = H, \ R_3 = n\text{-hexyl}; \ \text{or} \end{split}$$

 $\begin{array}{lll} & R_1 = & 2-ethylhexyloxy, \ R_2 = & H, \ R_3 = & methyl \\ & R_1 = & 2-ethylhexyloxy, \ R_2 = & H, \ R_3 = & phenyl \\ & R_1 = & 1-butyl, \ R_2 = & R_3 = & n-hexyl \\ & R_1 = & 2-ethylhexyloxy, \ R_2 = & H, \ R_3 = & n-hexyl. \end{array}$ 



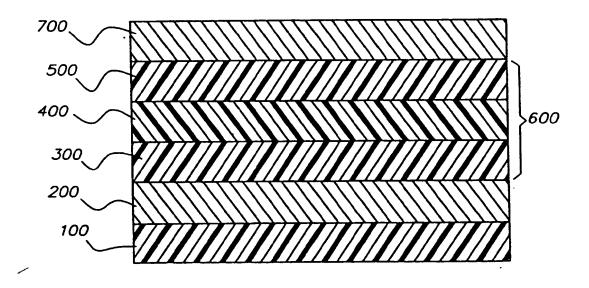


FIG. 2

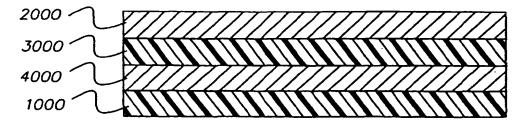


FIG. 3

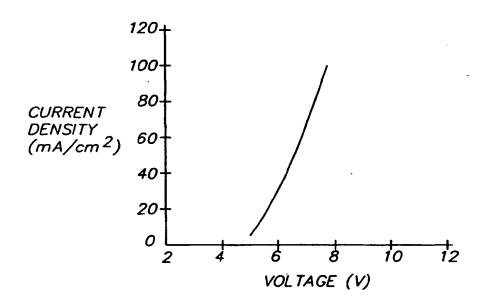


FIG. 6

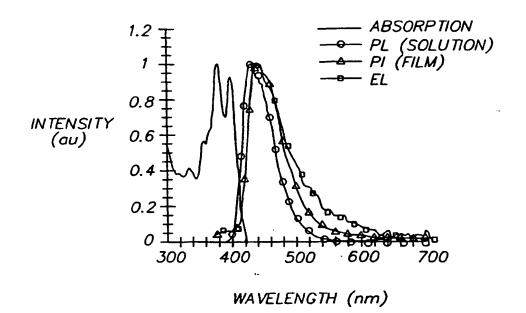


FIG. 4

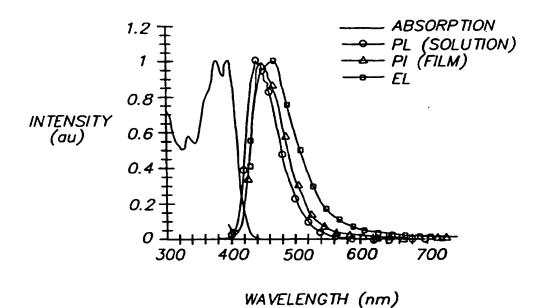


FIG. 5



# Europäisches Patentamt European Patent Office Office européen des brevets



(11) EP 1 094 101 A3

(12)

#### **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3: 31.03.2004 Bulletin 2004/14

(51) Int CL7: C09K 11/06, H05B 33/14

(43) Date of publication A2: 25.04.2001 Bulletin 2001/17

(21) Application number: 00203504.6

(22) Date of filing: 09.10.2000

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU

MC NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 20.10.1999 US 421980

(71) Applicant: EASTMAN KODAK COMPANY Rochester, New York 14650 (US) (72) Inventors:

- Shi, Jianmin, c/o Eastman Kodak Company Rochester, New York 14650-2201 (US)
- Zheng, Shiying, c/o Eastman Kodak Company Rochester, New York 14650-2201 (US)
- (74) Representative: Weber, Etienne Nicolas et al Kodak Industrie, Département Brevets, CRT, Zone Industrielle 71102 Chalon sur Saône Cedex (FR)

# (54) Electroluminescent devices having naphthylanthracene-based polymers

(57) An electroluminescent device comprises an anode, a cathode, and polymer luminescent materials disposed between the anode and cathode, the polymeric luminescent materials includes 9,10-di-(2-naphthyl)anthracene-based polymers of the following formula:

#### wherein:

R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are each individually hydrogen, or alkyl, or alkoxy of from 1 to 24 carbon atoms; aryl or substituted aryl of from 6 to 28 carbon atoms; or heteroaryl or substituted heteroaryl of from 4 to 40 carbons; or F, Cl, or Br; or a cyano group; or a nitro group;

X is a linking group; and

Y includes one or more comonomer units that are a substituted or unsubstituted alkyl, alkenyl, aryl, or heteroaryl or a conjugated group.



# EUROPEAN SEARCH REPORT

Application Number

EP 00 20 3504

\min ===	Citation of document with in	dication, where appropriate,	Relevant	CLASSIFICATION OF THE
ategory	of relevant passag		to claim	APPLICATION (Int.CI.7)
A	EP 0 681 019 A (TDK 8 November 1995 (19 * the whole documen	95-11-08)	1-10	C09K11/06 H05B33/14
A	US 5 935 721 A (CHE 10 August 1999 (199 * the whole documen	9-08-10)	1-10	·
				TECHNICAL FIELDS
				SEARCHED (Int.Cl.7)
				H05B
	The present search report has be	peen drawn up for all claims Date of completion of the sea	reh	Examiner
	MUNICH	4 February 20	i.	llio, M
X : par Y : par doc A : tecl	ATEGORY OF CITED DOCUMENTS tocularly relevant if taken alone ticularly relevant if combined with another of the same category nological background the written disclosure	T: theory or p E: earlier pals after the fă  D: document L: document	inciple underlying the igent document, but publing date cited in the application cited for other reasons	invention shed on, or

# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 00 20 3504

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

04-02-2004

	Patent docume cited in search re	nt port	Publication date		Patent fami member(s	ily )	Publication date
EP	0681019	A	08-11-1995	DE DE EP JP US	69511755 69511755 0681019 8012600 5635308	T2 A2 A	07-10-1999 13-01-2000 08-11-1995 16-01-1996 03-06-1997
US	5935721	A	10-08-1999	NONE			
							v,
				-			•.
						•	
			·				

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

3

FORM P0450

THIS PAGE BLANK (USPTO)